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Electronic Supporting Information

Trapping of the Putative 1,2-Dinitrosoarene Intermediate of Benzofuroxan Tautomerization by Coordination at Ruthenium, and Exploration of its Redox Non-Innocence

Siu-Chung Chan,[a] *Jason England,*[b] *Karl Wieghardt**[b] *and Chun-Yuen Wong**[a]

[a] Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, People's Republic of China.
E-mail: acywong@cityu.edu.hk

[b] Max-Planck-Institut für Chemische EnergieKonversion, Stiftstrasse 34–36, 45470 Mülheim an der Ruhr, Germany.
E-mail: karl.wieghardt@cec.mpg.de

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EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents were used as received, and solvents for reactions were purified by a PureSolv MD5 solvent purification system. $[Ru([9]aneS3)(dmso)Cl_2]$[1], $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$[2], $[Ru([14]aneS4)(dmso)Cl](PF_6)$[3] and $[Ru([9]aneS3)(ON^N)(CH_3CN)](ClO_4)$[4] were prepared according to literature procedures. Benzofuroxan was purchased from Sigma Aldrich while 5-methoxylbenzofuroxan and 5,6-dimethylbenzofuxan were synthesized from oxidative cyclization of 4-methoxy-2-nitroaniline and 4,5-dimethyl-2-nitroaniline respectively according to literature procedures.[5]

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on Bruker 400 DRX FT-NMR spectrometers. Peak positions were calibrated with solvent residue peaks as internal standard. Electrospray ionization mass spectrometry (ESI-MS) was performed on a PE-SCIEX API 3000 triple quadrupole mass spectrometer. Infrared spectra were recorded as KBr plates on a Perkin-Elmer FTIR-1600 spectrophotometer. UV–visible spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analyses were done on an Elementar Vario EL analyzer. Cyclic voltammetry was performed with a CH Instrument Model 600C series electrochemical analyzer/workstation. All solutions were degassed with argon before experiments. The glassy carbon working electrode was polished with 0.05 μm alumina on a microcloth, sonicated for 5 min in deionized water, and rinsed with CH_3CN before use. An $Ag/AgNO_3$ (0.1 M in CH_3CN) electrode was used as the reference electrode, and the $E_{1/2}$ value of the ferrocenium/ferrocene couple (Fc^+/Fc^0) measured in the same solution was used as an internal reference. Thin-layer UV–vis spectroelectrochemistry was performed on an Agilent 8453 diode array spectrophotometer using a thin-layer quartz cell with a platinum-gauze working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode.

EPR samples of $\mathbf{1b}^-$ and $\mathbf{1c}^-$ were prepared by bulk electrolysis at –20˚C of 2 mM CH_3CN

solutions of **1b** and **1c**, respectively, containing 0.2 M $[Bu_4N]PF_6$ electrolyte. Complexes $\mathbf{2a}^-$ and $\mathbf{2b}^-$ were isolated as pure solids, so 0.25 mM EPR samples of these were prepared by straightforward dissolution in CH_2Cl_2. Continuous wave X-band EPR spectra were recorded for all complexes on a Bruker E500 ELEXSYS spectrometer with a standard Bruker cavity (ER4102ST) and an Oxford Instruments helium flow cryostat (ESR 910). Microwave frequencies were measured using a Hewlett-Packard frequency counter (HP5352B) and the field control was calibrated with a Bruker NMR field probe (ER035M). As a consequence of signal attenuation in fluid solution due to high solvent polarity, it was necessary to measure the spectra of $\mathbf{1b}^-$ and $\mathbf{1c}^-$ in Q-band EPR tubes inserted into X-band tubes. All spectral manipulation and simulations were performed using the Bruker XSOPHE Suite, with a spin Hamiltonian of the form $\hat{H} = g\ \mu_B\ B\ S + \Sigma a\ S\ I$, where the summation term is weighted over all naturally occurring isotopes of N and Ru and the other terms have their standard meanings. Satisfactory fits were achieved using Gaussian line shapes and the isotropic liquids model, $\sigma_v = a + bM_I + cM_I^2 + dM_I^3$, which accounts for molecular tumbling.

[Ru([9]aneS3)(ON^NO)(Cl)](ClO_4) (**1a–1c**(ClO_4)). 0.1 g (0.23 mM) of [Ru([9]aneS3)(dmso)Cl_2] and 3 eq. of the corresponding benzofuroxan were refluxed in $CHCl_3$ (40 ml) under argon for 14 hours. The initial yellow color suspension gradually changed to dark-green suspension. The reaction mixture was then evaporated to dryness. Deionized water (10 ml) was added and the resulting green solution was added into a saturated aqueous solution of $NaClO_4$ (2 ml) to afford green precipitates. (**Caution!** *Perchlorate salts are potentially explosive and should be handled with care and in small amounts*). The green precipitates were collected and washed with absolute ethanol followed by diethyl ether. The solid was then recrystallized by slow diffusion of diethyl ether into a nitromethane solution to afford dark-green crystals. Preparation of **1a**(Cl): after the reaction mixture was evaporated to dryness, acetone (5 ml) was added instead of water and the green solution was added into diethyl ether (100 ml) to afford green precipitates. Recrystallization by the same condition affords the dark-green crystals which are suitable for X-ray crystal diffraction

measurement.

The diamagnetic nature of [Ru([9]aneS3)(ON^NO)Cl]$^{+}$ (**1a–1c**) in solid state have been confirmed by magnetic susceptibility measurements. Notably, they do not show signals in the conventional aromatic region (7–8 ppm), although the ON^NO ligands are expected to display signals there. It is due to fluxional behavior of the complexes in solution. Variable temperature ^{1}H NMR of **1b** has been measured from 293 K down to 193 K in d^{6}-acetone, and all aromatic proton signals can be located and resolved at 193 K (Figure S1).

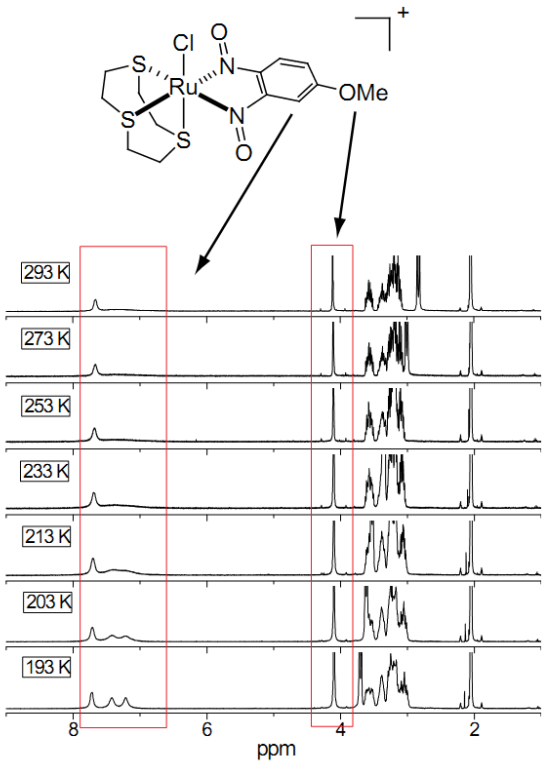

Figure S1. Variable temperature ^{1}H NMR spectra of **1b** from 293 K to 193 K in d^{6}-acetone.

1a(ClO_4). Yield: 0.056 g, 43 %. Anal. Calcd for $Ru_1C_{12}H_{16}N_2S_3Cl_2O_6$: C, 26.09; H, 2.92; N, 5.07. Found: C, 26.31; H, 3.01; N, 5.02. ^{1}H NMR (400 MHz, CD_3CN, 293 K): δ 2.79–2.87, 2.93–3.01, 3.11–3.14 (m, [9]aneS3). IR (KBr, cm^{-1}): ν_{NO} = 1375, 1383, ν_{Cl-O} = 1070. ESI-MS: *m/z* 453 [M^+].

1a(Cl)·CH_3NO_2. Yield: 0.045 g, 40 %. Anal. Calcd for $Ru_1C_{12}H_{16}N_2S_3Cl_2O_2 \cdot CH_3NO_2$: C, 28.42; H, 3.49; N, 7.65. Found: C, 28.20; H, 3.52; N, 7.38. ^{1}H NMR (400 MHz, CD_3CN, 293 K): δ 2.82–2.90, 2.94–3.02, 3.11–3.16 (m, [9]aneS3). IR (KBr, cm^{-1}): ν_{NO} = 1378, 1383, ν_{Cl-O} = 1068. ESI-MS: *m/z* 453 [M^+].

1b(ClO_4). Yield: 0.066 g, 49 %. Anal. Calcd for $Ru_1C_{13}H_{18}N_2S_3Cl_2O_7$: C, 26.81; H, 3.12; N, 4.81. Found: C, 26.83; H, 3.15; N, 4.67. ^{1}H NMR (400 MHz, d^6-Acetone, 293 K): δ 3.07–3.43, 3.51–3.62 (m, 12H, [9]aneS3); 4.11 (s, 3H, MeO); 7.66 (s, 1H, ON^NO). ^{1}H NMR (400 MHz, d^6-Acetone, 193 K): δ 3.00–3.29, 3.35–3.43, 3.50–3.64 (m, 12H, [9]aneS3); 4.11 (s, 3H, MeO); 7.21–7.42 (m, 2H, ON^NO); 7.72 (s, 1H, ON^NO). IR (KBr, cm^{-1}): ν_{NO} = 1389, ν_{Cl-O} = 1081. ESI-MS: *m/z* 483 [M^+].

1c(ClO_4). Yield: 0.065 g, 49 %. Anal. Calcd for $Ru_1C_{14}H_{20}N_2S_3Cl_2O_6$: C, 28.97; H, 3.47; N, 4.83. Found: C, 29.11; H, 3.71; N, 4.81. ^{1}H NMR (400 MHz, CD_3CN, 293 K): δ 2.14 (s, 6H, Me_2); 2.77–2.86, 2.90–3.00, 3.08–3.16 (m, 12H, [9]aneS3). IR (KBr, cm^{-1}): ν_{NO} = 1365, ν_{Cl-O} = 1086. ESI-MS: *m/z* 481 [M^+].

$[Ru(bpy)_2(ON^NO)](PF_6)$ (**2a**$^-$**–2b**$^-$(PF_6)). 0.1 g (0.13 mM) of $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ and 1.1 eq. of corresponding benzofuroxan were refluxed in acetone (10 ml) under argon for 14 hours. The intial organge-yellow solution gradually changed to greenish-brown solution. The reaction mixture was then added to 150 ml diethyl ether to afford greenish-brown precipitates which correspond to the mixture of $[Ru(bpy)_2(ON^NO)]^{2+}$ (**2a**, **2b**) and $[Ru(bpy)_2(ON^NO)^{\bullet-}]^+$ (**2a**$^-$, **2b**$^-$).

Complexes **2a** and **2b** could be reduced to **2a**$^{-}$ and **2b**$^{-}$ by filtering through a short pad of basic alumina using 20 % acetone/dichloromethane as eluent. The initial greenish-brown solution changed to orange-brown after discharging into the basic alumina and the resulting orange-brown solution was eluted out using the eluent as aforementioned. The orange-brown solution was concentrated to *ca.* 3 ml and then added dropwise by filtration into a diethyl ether solution (150 ml) to afford the orange-brown precipitate. The solid was then recrystallized by slow diffusion of diethyl ether into a dichloromethane solution under argon to afford the brown crystals. Although singe crystal of **2b** is obtained, attempt to get pure **2a** and **2b** for further analysis were unsuccessful. Therefore, only the x-ray crystal data of **2b** is reported.

2a^{-}$(PF_6)\cdot CH_2Cl_2$. Yield: 0.045 g, 51 %. Anal. Calcd for $Ru_1C_{26}H_{20}N_6O_2P_1F_6\cdot CH_2Cl_2$: C, 41.60; H, 2.84; N, 10.78. Found: C, 41.39; H, 2.68; N, 11.01. IR (KBr, cm^{-1}): ν_{NO} = 1239, ν_{P-F} = 841. ESI-MS: *m/z* 549 [M^+].

2b^{-}$(PF_6)\cdot CH_2Cl_2$. Yield: 0.052 g, 55 %. Anal. Calcd for $Ru_1C_{27}H_{22}N_6O_3P_1F_6\cdot CH_2Cl_2$: C, 41.54; H, 2.99; N, 10.38. Found: C, 41.60; H; 2.94; N, 10.56. IR (KBr, cm^{-1}): ν_{NO} = 1218, ν_{P-F} = 841. ESI-MS: *m/z* 579 [M^+].

[Ru([14]aneS4)(PhNO)Cl](PF_6). 0.1 g (0.16 mM) of [Ru([14]aneS4)(dmso)Cl](PF_6) was reacted with 1.5 eq. of nitrosobenzene in methanol. The initial yellow solution gradually changed to reddish-brown solution. The reddish-brown solution was concentrated to *ca*. 2 ml and saturated aqueous solution of NH_4PF_6 (2 ml) was added to afford the brown precipitates. The precipitates are filtered and washed with absolute ethanol followed by diethyl ether. The solid was then recrystallized by slow diffusion of diethyl ether into a nitromethane solution to afford the reddish-brown crystals.

[Ru([14]aneS4)(PhNO)Cl](PF$_6$). Yield: 0.081 g, 77 %. Anal. Calcd for $Ru_1C_{16}H_{25}N_1S_4O_1Cl_1P_1F_6$: C, 29.25; H, 3.84; N, 2.13. Found: C, 29.56; H, 3.97; N, 2.33. ^{1}H NMR (400 MHz, d^6-Acetone): δ 1.42–1.52, 1.71–1.98, 2.23–2.65, 2.76–2.97, 3.20–3.77 (m, 20H, [14]aneS4); 7.52–7.59 (m, 2H, PhNO), 7.78–7.86 (t, 1H, 6.4 Hz, PhNO), 8.49–8.53 (d, 2H, J = 6.6 Hz, PhNO). IR (KBr, cm^{-1}): ν_{NO} = 1368, ν_{P-F} = 841. ESI-MS: *m/z* 512 [M$^+$].

X-ray Crystallography. X-ray diffraction data for **1a**(Cl)·CH_3NO_2, **1b**(ClO_4), **2b**(PF_6)$_2$, **2a**$^-$(PF_6)·CH_2Cl_2 and **2b**$^-$(PF_6)·CH_2Cl_2 were collected on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer with either Cu Kα radiation (λ = 1.54178 Å) or Mo Kα radiation (λ = 0.71073 Å) at either 133 K or 173 K. The data were processed using CrysAlis.[7] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97[8] within WinGX[9]. All non-hydrogen atoms were refined anisotropically in the final stage of the least-squares refinement. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms. Disorder of the Cl^- in **1a**(Cl)·CH_3NO_2 and PF_6^-in **2b**(PF_6)$_2$ were observed, and split models were applied to them. CCDC 994514–994518 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methodology. DFT calculations were performed on complexes **1a–1c**, **2a**, and **2b** (S = 0, spin-restricted Kohn–Sham solutions) and **1a**$^-$**–1c**$^-$, **2a**$^-$, and **2b**$^-$ (S = 1/2, spin-unrestricted Kohn–Sham solutions) using the ORCA software package (version 3.0.0)[10]. Their electronic ground states were optimized using the TPSSh functional[11] accompanied with (i) the zero-order regular approximation (ZORA)[12] to account for relativistic effects, (ii) the conductor-like screening model (COSMO)[13] to model solvation in CH_3CN, and (iii) empirical dispersion correction by Grimme.[14] The def2-SVP basis sets were used for the C and H atoms, while the

def2-TZVP basis sets were used for the Ru, Cl, S, O and N atoms.[15] Auxiliary basis sets, used to expand the electron density in the calculations, were chosen to match the orbital basis sets. The combination of the resolution of the identity and the "chain of spheres exchange" algorithms (RIJCOSX)[16] was used to accelerate all calculations. Tight SCF convergence criteria (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the density charge, and 1×10^{-7} in the maximum element of the DIIS error vector) were used throughout.

X-ray Crystallography

Table S1. Crystallography data

	1a(Cl)·CH_3NO_2	**1b**(ClO_4)	**2b**(PF_6)$_2$	**2a**$^-$(PF_6)·CH_2Cl_2	**2b**$^-$(PF_6)·CH_2Cl_2
Chem. Formula	$C_{13}H_{19}Cl_2N_3O_4RuS_3$	$C_{13}H_{18}Cl_2N_2O_7RuS_3$	$C_{27}H_{22}F_{12}N_6O_3P_2Ru$	$C_{27}H_{22}Cl_2F_6N_6O_2PRu$	$C_{28}H_{24}Cl_2F_6N_6O_3PRu$
Fw	549.34	582.44	869.52	779.45	809.47
Crystal size, mm^3	0.28 × 0.18 × 0.09	0.81 × 0.52 × 0.03	0.36 × 0.11 × 0.02	0.79 × 0.26 × 0.02	0.41 × 0.21 × 0.03
Space group	Pn	P21/c	P21/c	P21/c	Pbcn
a, Å	11.7724(2)	16.4668(3)	14.0590(2)	13.5677(7)	14.1173(2)
b, Å	13.4968(3)	19.6645(3)	14.2401(2)	14.3521(8)	15.5837(2)
c, Å	12.2285(3)	12.6551(3)	15.4559(2)	15.5809(7)	28.1669(5)
α, deg	90.00	90.00	90.00	90.00	90.00
β, deg	110.968(2)	106.281(2)	91.983(1)	95.869(5)	90.00
γ, deg	90.00	90.00	90.00	90.00	90.00
V, $Å^3$	1814.32(7)	3933.53(13)	3092.44(7)	2998.7(3)	6196.71(16)
Z	2	8	4	4	8
T, K	133(2)	133(2)	173(2)	173(2)	173(2)
ρ calcd, g cm^{-3}	1.900	1.967	1.868	1.726	1.735
refl. collected / $2\theta_{max}$	11507 / 134.98	21119 / 55.00	12045 / 134.98	13141 / 53.00	23669 / 135.00
unique refl. / I>2σ(I)	4796 / 4747	8727 / 7553	5556 / 5259	6151 / 4905	5585 / 4846
No. of params / restr.	455 / 2	507 / 0	498 / 0	406 / 0	425 / 0
λ, Å / μ(Kα), mm^{-1}	1.54178 / 13.089	0.71073 / 1.428	1.54178 / 6.161	0.71073 / 0.830	1.54178 / 6.885
R_1[a] / GooF[b]	0.0235 / 1.025	0.0272 / 1.131	0.0382 / 1.073	0.0471 / 1.049	0.0482 / 1.053
wR_2[c] (I>2σ(I))	0.0634	0.0567	0.0937	0.1198	0.1333
residual density, $eÅ^{-3}$	+ 0.608 / – 0.538	+ 0.904 / – 0.581	+ 1.000 / – 0.552	+ 1.056 / – 0.782	+ 0.867 / – 0.777

[a] $R_1 = \Sigma||F_o| - |F_c|□|□ / \Sigma|F_o|$. [b] GooF = $\{ \Sigma[w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$. [c] $wR_2 = \{ \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] \}^{1/2}$

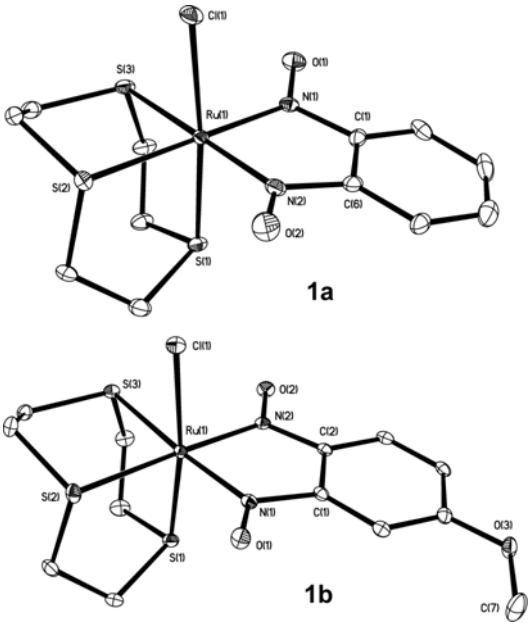

Figure S2. Perspective views of the cations in **1a**(Cl)·CH_3NO_2 and **1b**(ClO_4). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30 % level.

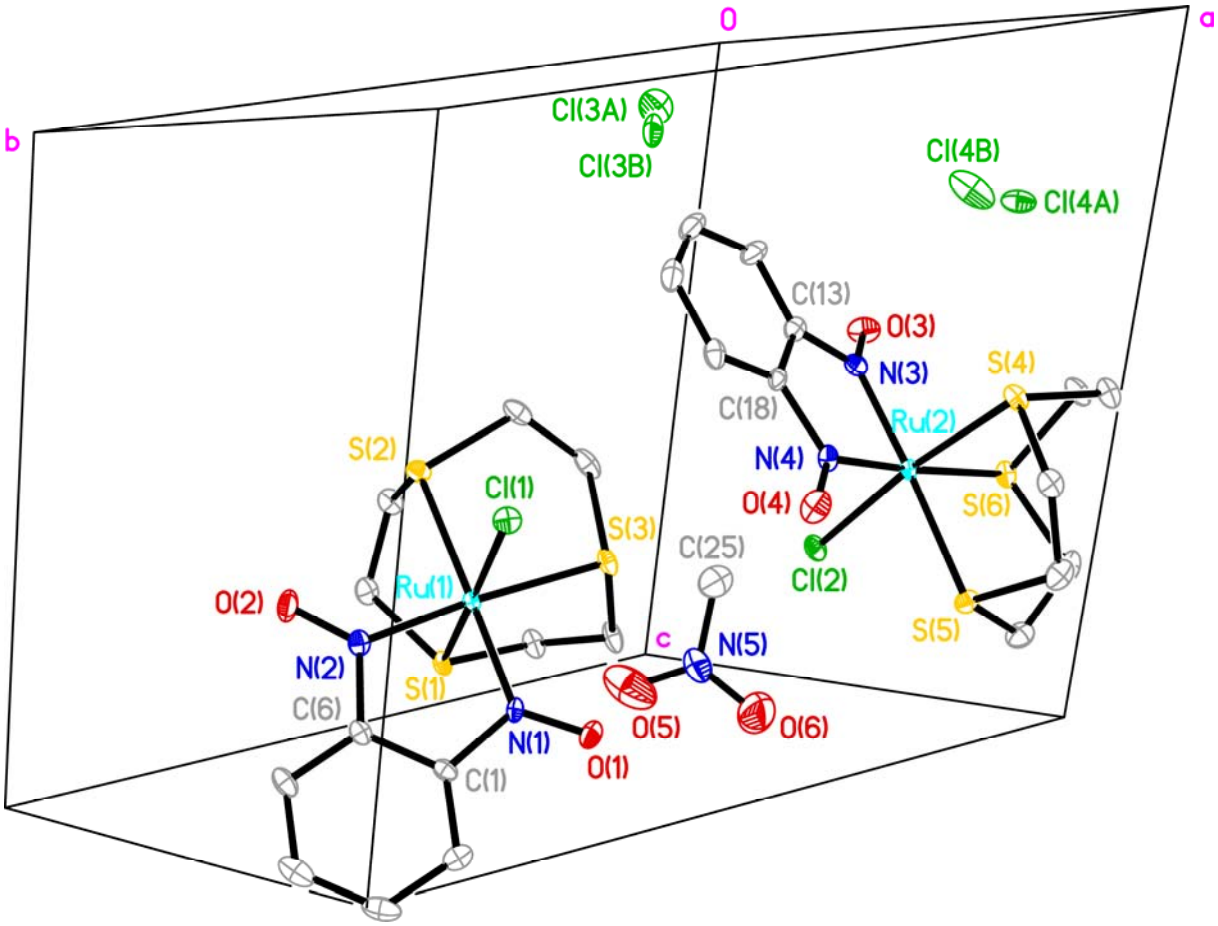

Figure S3. The asymmetric unit of **1a**(Cl)·CH_3NO_2. The Cl(3) and Cl(4) are disorder over two positions.

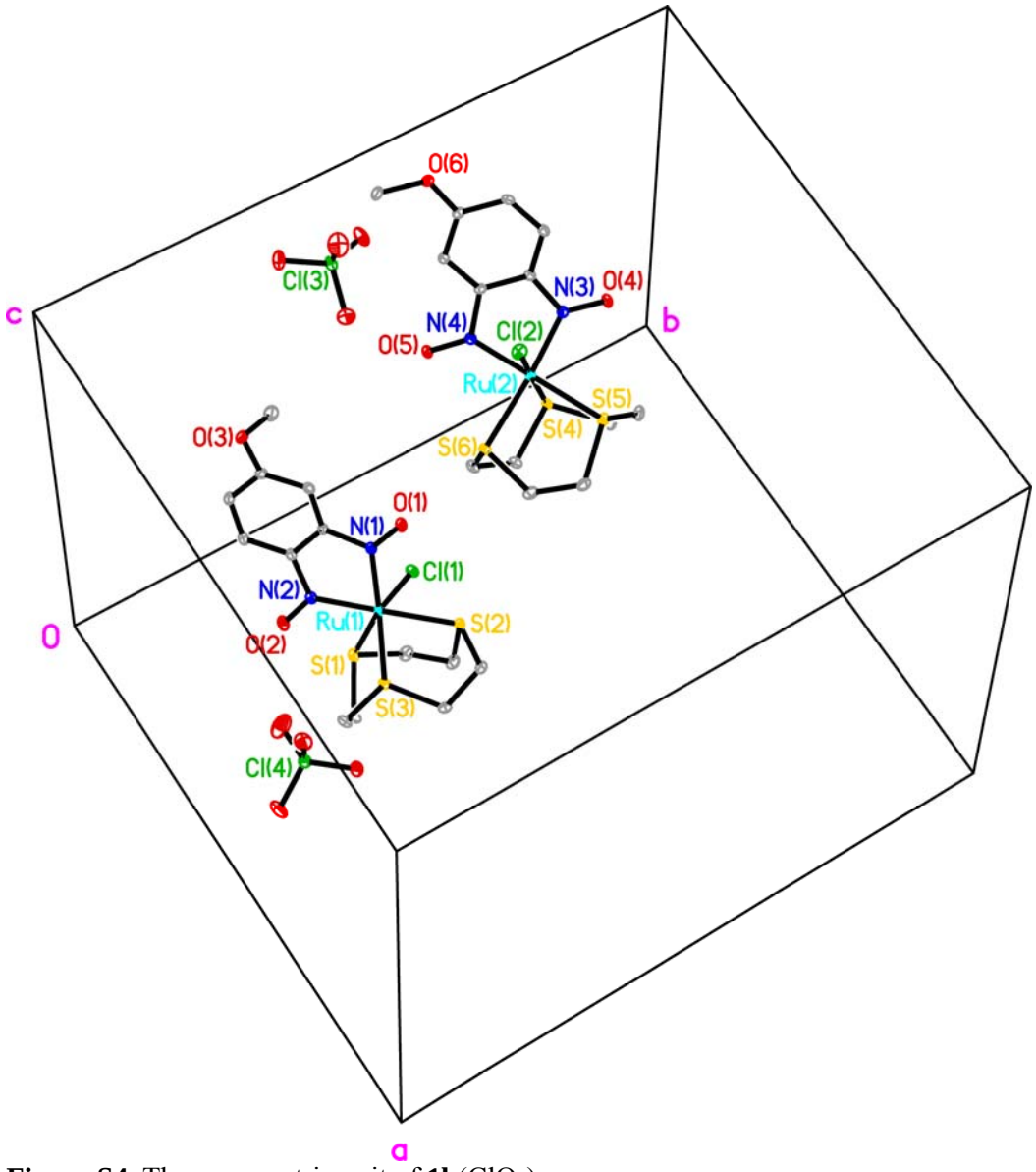

Figure S4. The asymmetric unit of **1b**(ClO_4).

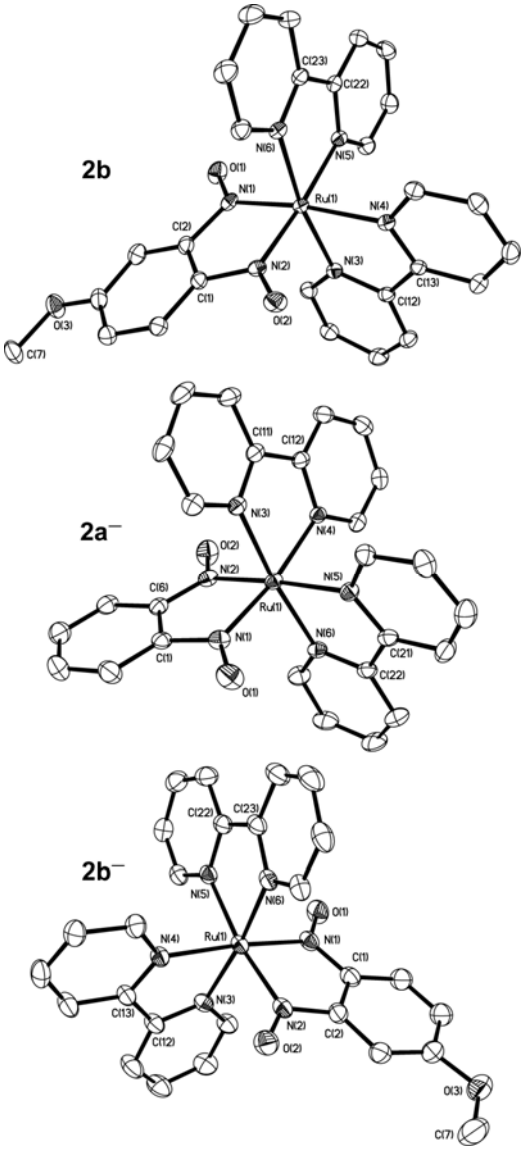

Figure S5. Perspective views of the cations in **2b**$(PF_6)_2$, **2a**$^{-}(PF_6)\cdot CH_2Cl_2$ and **2b**$^{-}(PF_6)\cdot CH_2Cl_2$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30 % level.

Electrochemical Studies

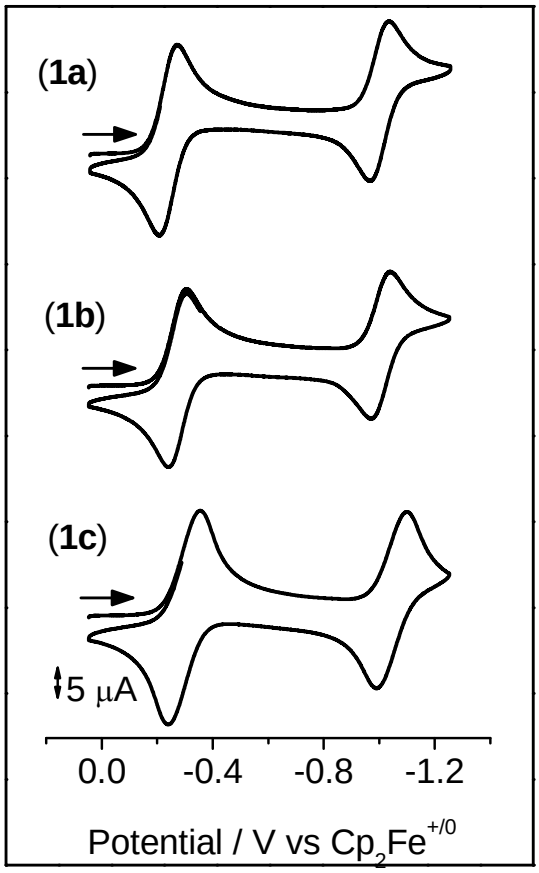

Figure S6. Cyclic voltammogram of **1a** (Top), **1b** (Middle) and **1c** (Bottom) (supporting electrolyte: 0.1 M $[Bu_4N]PF_6$ in CH_3CN; scan rate = 100 mVs^{-1}).

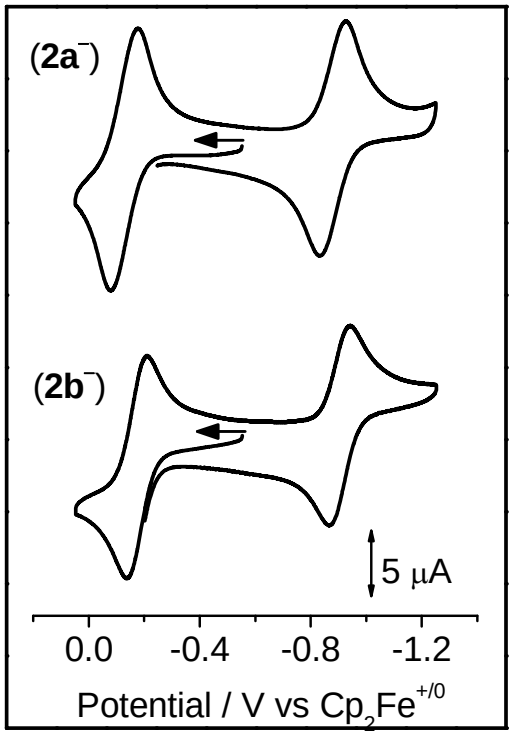

Figure S7. Cyclic voltammogram of $\mathbf{2a}^-$ (Top) and $\mathbf{2b}^-$ (Bottom) (supporting electrolyte: 0.1 M $[Bu_4N]PF_6$ in CH_3CN; scan rate = 100 mVs^{-1}).

EPR Studies

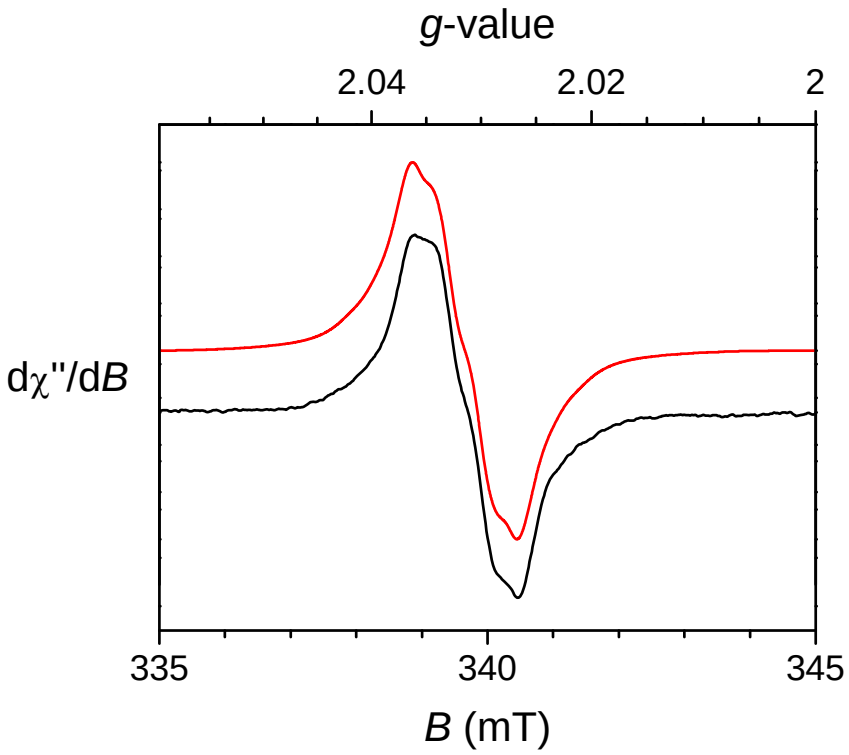

Figure S8. Perpendicular mode X-band EPR spectrum (black line) and spectral simulation (red line) of **1b**$^{-}$, recorded at room temperature in CH_3CN solution containing 0.2 M NBu_4PF_6. Conditions: frequency 9.66 GHz; power 1.0 mW; modulation 0.1 mT. Simulations were performed using the parameters listed in Table S4.

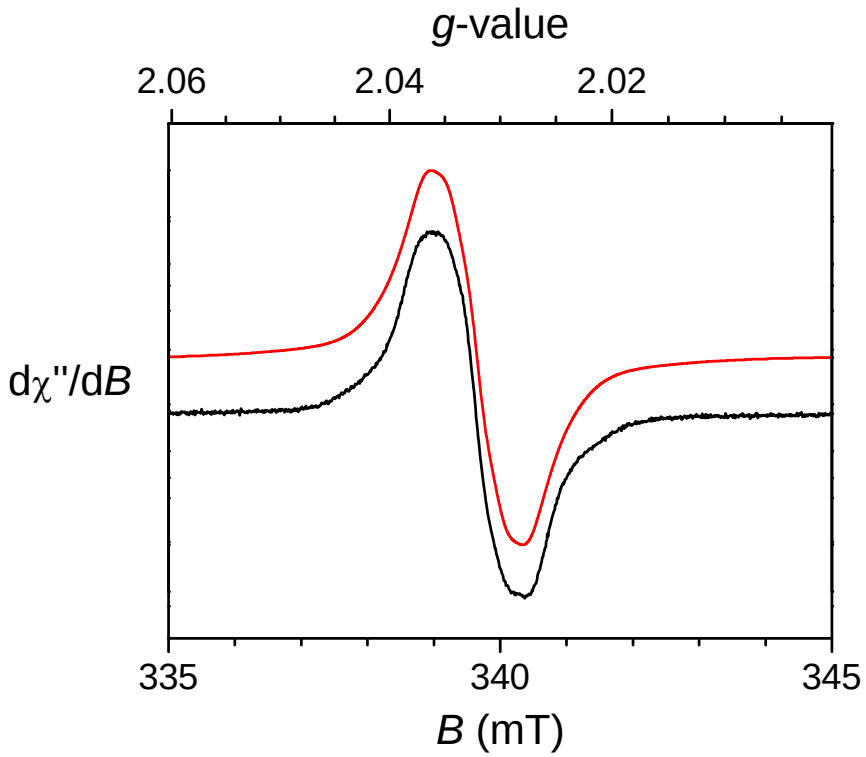

Figure S9. Perpendicular mode X-band EPR spectrum (black line) and spectral simulation (red line) of **1c**$^{-}$, recorded at room temperature in CH_3CN solution containing 0.2 M NBu_4PF_6. Conditions: frequency 9.66 GHz; power 1.0 mW; modulation 0.2 mT. Simulations were performed using the parameters listed in Table S4.

Theoretical Calculation

Table S2. Selected bond length and angle from DFT calculation with TPSSh functional accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

complex	**1a**	**1a$^-$**	**1b**	**1b$^-$**	**1c**	**1c$^-$**	**2a**	**2a$^-$**	**2b**	**2b$^-$**
Ru–N	1.960, 1.967	1.992, 2.000	1.960, 1.978	1.993, 2.007	1.963, 1.973	1.997, 2.003	1.959, 1.970	1.994, 2.005	1.953, 1.983	2.001, 2.006
N–O	1.228, 1.229	1.259, 1.260	1.229, 1.233	1.265, 1.271	1.229, 1.231	1.267, 1.268	1.227, 1.228	1.265, 1.266	1.228, 1.232	1.264, 1.271
N–C	1.438, 1.440	1.390, 1.391	1.417, 1.444	1.386	1.434	1.388, 1.389	1.440, 1.441	1.390, 1.392	1.417, 1.448	1.385, 1.388
C–C	1.406	1.423	1.405	1.423	1.405	1.421	1.408	1.425	1.408	1.424
Ru–S_{eq}	2.367, 2.378	2.344, 2.351	2.368, 2.374	2.349, 2.358	2.365, 2.378	2.349, 2.356				
Ru–S_{ax}	2.344	2.295	2.343	2.304	2.342	2.305				
Ru–Cl	2.389	2.394	2.392	2.422	2.391	2.422				
Ru–N_{bpy} trans to NO							2.086, 2.091	2.080, 2.084	2.086, 2.093	2.079, 2.083
Ru–N_{bpy} cis to NO							2.066, 2.071	2.057, 2.061	2.065, 2.072	2.056, 2.061
C–C_{bpy}							1.468, 1.470	1.468, 1.469	1.469	1.468, 1.469
N–Ru–N	83.58	82.00	83.30	81.65	83.44	81.67	83.57	81.69	83.24	81.38

Table S3. Cartesian Coordinates of **1a** at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	2.567692	0.700335	-0.13242
C	3.745082	1.420119	-0.31111
H	3.722054	2.506441	-0.32702
C	4.939888	0.704955	-0.46201
H	5.872304	1.246253	-0.60081
C	4.946501	-0.69775	-0.4382
H	5.884305	-1.23443	-0.55738
C	3.758284	-1.41894	-0.26482
H	3.746104	-2.50536	-0.24335
C	2.573757	-0.70521	-0.11104
C	-1.59048	-1.70287	-2.01699
H	-2.05761	-1.77223	-3.00466
H	-0.78204	-2.43896	-1.96426
C	-2.60778	-1.89869	-0.91524
H	-2.98555	-2.92486	-0.93542
H	-3.46049	-1.22308	-1.0159
C	-3.12632	-0.59242	1.560691
H	-4.04794	-1.17909	1.618495
H	-2.7328	-0.45563	2.572324
C	-3.37598	0.733123	0.872575
H	-4.02304	1.359565	1.492993
H	-3.85925	0.608031	-0.09945
C	-1.99793	2.243477	-1.11238
H	-2.87538	2.895591	-1.16589
H	-1.10436	2.851718	-1.28603
C	-2.11581	1.111718	-2.10795
H	-2.064	1.497318	-3.13063
H	-3.05009	0.55629	-1.99905
Cl	0.096474	0.029015	2.717737
N	1.276833	1.302407	0.066188
N	1.28641	-1.31474	0.103058
O	1.213518	2.530122	0.066273
O	1.234895	-2.54128	0.118926
Ru	-0.15959	-0.00224	0.34261
S	-0.71922	-0.08602	-1.93203
S	-1.84847	-1.62788	0.744264
S	-1.80734	1.673812	0.620379

Table S4. Cartesian Coordinates of **1b** at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	1.358286	7.018874	1.275314
C	1.687632	5.700229	1.632859
C	0.671063	4.763214	1.860042
H	0.926185	3.742513	2.130415
C	-0.65085	5.166552	1.743982
H	-1.46199	4.464857	1.918742
C	-0.97478	6.504522	1.407817
C	0.046277	7.445604	1.158557
H	-0.15617	8.475035	0.884245
C	-2.66488	8.157243	1.038753
H	-2.25375	8.843927	1.785752
H	-3.75441	8.162898	1.079146
H	-2.31989	8.425954	0.034999
C	4.904059	8.083173	-1.5867
H	5.227501	7.910736	-2.61823
H	3.955349	8.628366	-1.60885
C	5.964855	8.820006	-0.79892
H	6.080135	9.835013	-1.18898
H	6.935923	8.323709	-0.85584
C	7.077566	8.523657	1.804036
H	7.831417	9.258365	1.505229
H	6.855589	8.65892	2.866964
C	7.551289	7.116924	1.503967
H	8.395846	6.862248	2.150128
H	7.875243	7.005544	0.466648
C	6.353692	4.809413	0.336479
H	7.351939	4.360868	0.311839
H	5.622426	4.016054	0.519941
C	6.073916	5.554574	-0.94993
H	5.99978	4.85564	-1.78821
H	6.850043	6.28686	-1.18234
Cl	4.23006	7.669891	3.690328
N	2.488844	7.892543	1.063027
N	3.075117	5.437677	1.755278
O	2.250152	9.049782	0.726634
O	3.427889	4.301914	2.080479
O	-2.28146	6.797827	1.34968
Ru	4.210817	7.015273	1.390142
S	4.458277	6.449517	-0.87001
S	5.498128	8.967701	0.981274
S	6.232423	5.864564	1.831756

Table S5. Cartesian Coordinates of **1c** at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	2.568245	0.69271	-0.13022
C	3.751741	1.398248	-0.30245
H	3.72887	2.485556	-0.30911
C	4.96507	0.704767	-0.45679
C	4.969827	-0.71691	-0.43947
C	3.761179	-1.41418	-0.26791
H	3.745628	-2.50149	-0.24865
C	2.57179	-0.71199	-0.11314
C	-1.59555	-1.69454	-2.02416
H	-2.06606	-1.75665	-3.01074
H	-0.78965	-2.43385	-1.97813
C	-2.61043	-1.89402	-0.92064
H	-2.98997	-2.91951	-0.94446
H	-3.46242	-1.21675	-1.01678
C	-3.12461	-0.59861	1.559973
H	-4.04639	-1.18528	1.61605
H	-2.73027	-0.46589	2.571852
C	-3.374	0.729877	0.877208
H	-4.02071	1.354062	1.500251
H	-3.85761	0.608732	-0.09523
C	-1.99431	2.247305	-1.10256
H	-2.87138	2.900133	-1.15361
H	-1.10006	2.855565	-1.27262
C	-2.11146	1.120981	-2.10484
H	-2.0562	1.512546	-3.12508
H	-3.04741	0.567038	-2.00195
Cl	0.109585	0.013793	2.717732
N	1.284356	1.298792	0.069125
N	1.290222	-1.32017	0.097648
O	1.223853	2.528112	0.080406
O	1.235194	-2.54811	0.122389
Ru	-0.15866	-0.00389	0.341682
S	-0.71795	-0.08122	-1.93169
S	-1.84715	-1.63033	0.738293
S	-1.80424	1.670117	0.627961
C	6.227999	1.496919	-0.65336
H	6.262538	1.893866	-1.67708
H	6.254629	2.352864	0.028751
H	7.124369	0.893803	-0.49639
C	6.249096	-1.48838	-0.60798
H	6.714636	-1.26101	-1.57588
H	6.97406	-1.22161	0.171285
H	6.064292	-2.56479	-0.55568

Table S6. Cartesian Coordinates of **2a** at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	0.02909	-0.03542	0.044927
C	0.084922	-0.14853	1.430071
H	1.045682	-0.19145	1.935128
C	-1.12355	-0.19515	2.136473
H	-1.10503	-0.27657	3.220432
C	-2.3539	-0.141	1.464558
H	-3.27937	-0.1823	2.032901
C	-2.40706	-0.03548	0.069224
H	-3.35144	0.004437	-0.46636
C	-1.20518	0.020468	-0.62985
C	0.643388	3.119611	-1.4244
H	1.025483	2.583091	-0.56231
C	0.369837	4.481809	-1.36693
H	0.537582	5.022569	-0.44035
C	-0.11622	5.117145	-2.51172
H	-0.34758	6.178635	-2.50188
C	-0.3017	4.372189	-3.67585
H	-0.67475	4.849636	-4.57599
C	-0.00883	3.006554	-3.67505
C	-0.16126	2.130772	-4.84527
C	-0.59428	2.573432	-6.09716
H	-0.84831	3.616974	-6.25324
C	-0.70143	1.659712	-7.1456
H	-1.04055	1.989947	-8.1237
C	-0.37272	0.322657	-6.91549
H	-0.44343	-0.42453	-7.70031
C	0.053288	-0.05446	-5.64442
H	0.317529	-1.08219	-5.41787
C	3.450913	1.626692	-3.34868
H	2.927909	2.538021	-3.07909
C	4.784949	1.645053	-3.74678
H	5.316524	2.590651	-3.79596
C	5.40505	0.438242	-4.07574
H	6.443641	0.414893	-4.39294
C	4.670138	-0.74458	-3.99838
H	5.13143	-1.69301	-4.25341
C	3.334119	-0.69469	-3.59491
C	2.465785	-1.87363	-3.48642
C	2.877528	-3.17872	-3.76653
H	3.896973	-3.37253	-4.08336
C	1.969235	-4.22877	-3.64116
H	2.280645	-5.24703	-3.8585
C	0.660288	-3.95151	-3.24
H	-0.08181	-4.73646	-3.13035
C	0.306691	-2.63364	-2.97268
H	-0.69713	-2.36844	-2.65787
N	1.188762	0.022689	-0.80834

N	-1.1071	0.155414	-2.05968
N	0.455935	2.401399	-2.5466
N	0.156056	0.825641	-4.63754
N	2.745697	0.488055	-3.27463
N	1.185759	-1.62209	-3.09337
O	2.286325	-0.17516	-0.29532
O	-2.15045	0.219026	-2.7015
Ru	0.748641	0.356166	-2.68838

Table S7. Cartesian Coordinates of **2b** at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	10.74639	8.182193	4.708411
C	10.41585	9.360842	5.403761
C	9.582942	9.355998	6.509206
H	9.357504	10.28991	7.012829
C	9.05149	8.1142	6.92332
C	9.396293	6.920342	6.239451
H	8.975359	5.983385	6.593711
C	10.2391	6.948904	5.14006
H	10.50291	6.0397	4.607504
C	7.785875	9.154094	8.671884
H	7.264774	9.838903	7.99457
H	7.104455	8.787564	9.439477
H	8.649376	9.643796	9.132471
C	14.40102	9.402043	4.754048
H	13.92053	8.431426	4.689384
C	15.61239	9.570379	5.415795
H	16.09015	8.714658	5.882598
C	16.18247	10.84484	5.461351
H	17.12656	11.0131	5.971598
C	15.52814	11.90405	4.834073
H	15.95976	12.89948	4.850579
C	14.31569	11.67484	4.179318
C	13.55955	12.70961	3.462301
C	13.98126	14.03525	3.333712
H	14.90754	14.36346	3.793545
C	13.20312	14.9308	2.60024
H	13.52331	15.96268	2.483614
C	12.0166	14.48055	2.018572
H	11.3791	15.14178	1.439218
C	11.64704	13.14937	2.192889
H	10.73025	12.75628	1.766482
C	14.09122	9.695868	1.058564
H	14.75134	9.717342	1.919156
C	14.58229	9.484122	-0.22752
H	15.64798	9.337088	-0.37712
C	13.68468	9.467703	-1.29625
H	14.03413	9.309652	-2.31314
C	12.32604	9.653039	-1.04161
H	11.60967	9.640873	-1.85709
C	11.89708	9.856328	0.272424
C	10.49108	10.05114	0.652733
C	9.426016	10.01551	-0.25034
H	9.611388	9.836655	-1.3048
C	8.123315	10.20179	0.211698
H	7.288278	10.17225	-0.48291
C	7.911765	10.42628	1.573286
H	6.917116	10.58056	1.980959

C	9.01096	10.45596	2.424373
H	8.892155	10.63693	3.487684
N	11.58059	8.363625	3.577981
N	11.02055	10.56481	4.872597
N	13.76784	10.42771	4.155422
N	12.39874	12.28786	2.894583
N	12.78526	9.882422	1.301215
N	10.26717	10.27322	1.977949
O	11.93233	7.367525	2.943994
O	10.88895	11.59778	5.523493
O	8.208526	7.973079	7.950865
Ru	11.95392	10.27012	3.182011

Table S8. Cartesian Coordinates of **1a**$^{-}$ at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	2.557935	0.710062	-0.13271
C	3.767443	1.416729	-0.29276
H	3.745238	2.503284	-0.3118
C	4.951997	0.706607	-0.41603
H	5.891706	1.241793	-0.53488
C	4.95449	-0.71166	-0.39196
H	5.896182	-1.24743	-0.49147
C	3.772244	-1.42116	-0.24551
H	3.753574	-2.50782	-0.22614
C	2.560492	-0.71355	-0.10886
C	-1.61677	-1.69356	-2.02892
H	-2.09766	-1.75698	-3.01065
H	-0.80642	-2.42843	-1.98444
C	-2.6173	-1.90215	-0.91258
H	-2.98734	-2.93135	-0.92662
H	-3.47646	-1.23246	-1.00178
C	-3.11299	-0.59703	1.564035
H	-4.03279	-1.18622	1.630761
H	-2.70919	-0.45867	2.571852
C	-3.37333	0.733023	0.884805
H	-4.01716	1.354882	1.513446
H	-3.86735	0.605909	-0.08214
C	-2.02936	2.24434	-1.11643
H	-2.91235	2.890085	-1.16076
H	-1.13693	2.853034	-1.29589
C	-2.14411	1.111925	-2.11322
H	-2.09881	1.49722	-3.13642
H	-3.07696	0.55412	-1.99919
Cl	0.18788	0.043149	2.703381
N	1.309283	1.305215	0.011053
N	1.314267	-1.30943	0.055486
O	1.224668	2.568414	-0.02818
O	1.236414	-2.57277	0.043555
Ru	-0.17077	0.005099	0.310405
S	-0.73808	-0.07911	-1.92423
S	-1.82783	-1.61803	0.735063
S	-1.80125	1.671543	0.612178

Table S9. Cartesian Coordinates of **1b**$^{-}$ at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	1.363755	7.03853	1.255066
C	1.693559	5.703986	1.621019
C	0.660219	4.772158	1.868032
H	0.921242	3.752788	2.138508
C	-0.65546	5.174278	1.772835
H	-1.46901	4.479324	1.965823
C	-0.97897	6.520554	1.428427
C	0.02103	7.449898	1.159159
H	-0.18515	8.477315	0.881336
C	-2.68522	8.156626	1.08489
H	-2.25872	8.849087	1.819724
H	-3.77495	8.175885	1.139102
H	-2.35227	8.427882	0.076285
C	4.943615	8.072736	-1.60616
H	5.285164	7.896004	-2.63136
H	3.994101	8.616335	-1.63906
C	5.986377	8.820544	-0.80306
H	6.100343	9.837711	-1.18811
H	6.961795	8.330439	-0.8465
C	7.064284	8.523552	1.810037
H	7.820164	9.260033	1.519687
H	6.827729	8.659182	2.870241
C	7.548366	7.115372	1.526304
H	8.383967	6.866907	2.186735
H	7.890257	7.004297	0.494111
C	6.384955	4.81151	0.333302
H	7.388578	4.373845	0.319954
H	5.654803	4.014609	0.506923
C	6.108685	5.555434	-0.95577
H	6.042892	4.857292	-1.79554
H	6.886094	6.28953	-1.1808
Cl	4.146118	7.672673	3.678604
N	2.444385	7.871106	1.008485
N	3.048303	5.423306	1.704424
O	2.223185	9.063291	0.628963
O	3.413979	4.250792	2.005438
O	-2.30701	6.803042	1.393195
Ru	4.218754	6.998213	1.353046
S	4.486813	6.449485	-0.86867
S	5.484641	8.950757	0.972061
S	6.218164	5.861873	1.829754

Table S10. Cartesian Coordinates of **1c**$^{-}$ at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	2.557239	0.706405	-0.16491
C	3.771352	1.405746	-0.31359
H	3.748633	2.493512	-0.31587
C	4.970606	0.717253	-0.44452
C	4.973087	-0.71971	-0.4397
C	3.775971	-1.4112	-0.30494
H	3.756542	-2.49902	-0.29957
C	2.559709	-0.71493	-0.16045
C	-1.65859	-1.66712	-2.05452
H	-2.15859	-1.71177	-3.02778
H	-0.85046	-2.40545	-2.03789
C	-2.63862	-1.89183	-0.92292
H	-3.00902	-2.92076	-0.94448
H	-3.49926	-1.22109	-0.98677
C	-3.09153	-0.62268	1.579417
H	-4.01038	-1.21288	1.651577
H	-2.67225	-0.49914	2.582809
C	-3.36227	0.71715	0.923984
H	-3.99488	1.330698	1.572026
H	-3.87266	0.604157	-0.03618
C	-2.05362	2.254893	-1.07861
H	-2.93946	2.898155	-1.09715
H	-1.16635	2.868868	-1.26527
C	-2.18287	1.136452	-2.08934
H	-2.15472	1.536069	-3.10766
H	-3.11346	0.576367	-1.96791
Cl	0.247597	0.003931	2.67134
N	1.311778	1.300845	-0.01595
N	1.316465	-1.31438	-0.00713
O	1.225598	2.565431	-0.04321
O	1.237042	-2.57846	-0.0408
Ru	-0.16941	-0.00366	0.285384
S	-0.77273	-0.05679	-1.93898
S	-1.81891	-1.63033	0.714492
S	-1.79295	1.65727	0.637442
C	6.268492	1.464922	-0.59113
H	6.761169	1.21471	-1.54073
H	6.10377	2.546233	-0.56117
H	6.970952	1.197869	0.209483
C	6.273702	-1.46433	-0.57855
H	6.777494	-1.20492	-1.51962
H	6.966265	-1.20378	0.23305
H	6.110222	-2.54608	-0.55971

Table S11. Cartesian Coordinates of **2a**$^-$ at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	0.065957	-0.02805	0.003931
C	0.105083	-0.16111	1.406874
H	1.069226	-0.20686	1.905572
C	-1.08763	-0.2204	2.109599
H	-1.0709	-0.31459	3.193371
C	-2.33394	-0.16082	1.433483
H	-3.25585	-0.21057	2.008627
C	-2.38981	-0.0405	0.054185
H	-3.3344	0.004495	-0.48093
C	-1.18503	0.031744	-0.6758
C	0.656582	3.11568	-1.4476
H	1.068715	2.569784	-0.60529
C	0.355145	4.471361	-1.36453
H	0.532562	5.003818	-0.4345
C	-0.17224	5.113758	-2.48769
H	-0.42724	6.169528	-2.45646
C	-0.36726	4.379859	-3.65718
H	-0.772	4.859998	-4.54259
C	-0.04288	3.020293	-3.68078
C	-0.1969	2.155038	-4.85827
C	-0.66155	2.601011	-6.09933
H	-0.94212	3.640381	-6.23878
C	-0.76494	1.697656	-7.15635
H	-1.12772	2.029453	-8.1256
C	-0.39943	0.365838	-6.94433
H	-0.46427	-0.37436	-7.73676
C	0.056546	-0.01282	-5.68432
H	0.351904	-1.03525	-5.47089
C	3.489435	1.605282	-3.38168
H	2.963624	2.525752	-3.1493
C	4.835046	1.604508	-3.73863
H	5.376906	2.544289	-3.79415
C	5.456229	0.384916	-4.02039
H	6.504099	0.346087	-4.30494
C	4.707327	-0.78808	-3.93911
H	5.166775	-1.74669	-4.15827
C	3.358745	-0.71728	-3.57694
C	2.475857	-1.88475	-3.46504
C	2.879749	-3.20124	-3.70735
H	3.904192	-3.41288	-3.99684
C	1.957708	-4.23827	-3.57791
H	2.26092	-5.26536	-3.76424
C	0.643873	-3.9339	-3.21101
H	-0.10926	-4.70829	-3.09833
C	0.300262	-2.60538	-2.98319
H	-0.7052	-2.31431	-2.69652
N	1.191361	0.054142	-0.81071

N	-1.10568	0.154572	-2.05815
N	0.460236	2.405433	-2.57404
N	0.156133	0.856248	-4.66602
N	2.768015	0.475911	-3.30059
N	1.191258	-1.60407	-3.10762
O	2.335266	-0.07905	-0.28781
O	-2.17548	0.188249	-2.73362
Ru	0.769701	0.37405	-2.73343

Table S12. Cartesian Coordinates of **2b**$^{-}$ at the TPSSh optimized geometry accompanied with empirical dispersion correction and conductor-like screening model (COSMO, solvent = CH_3CN).

Atom	Coordinates in Å		
	X	Y	Z
C	10.79909	8.209622	4.668111
C	10.46406	9.404307	5.366544
C	9.62579	9.369201	6.496981
H	9.386802	10.30305	6.993439
C	9.128075	8.137672	6.913561
C	9.484389	6.932987	6.234338
H	9.078085	5.994851	6.604111
C	10.30883	6.967197	5.13125
H	10.58153	6.060371	4.598962
C	7.844352	9.150415	8.65831
H	7.312098	9.822779	7.974805
H	7.168694	8.792675	9.436423
H	8.697757	9.668943	9.109335
C	14.39966	9.401147	4.710729
H	13.95227	8.424047	4.55822
C	15.55606	9.569062	5.465696
H	16.02872	8.703824	5.92073
C	16.0789	10.85589	5.623101
H	16.97601	11.02468	6.212493
C	15.43659	11.92527	5.001178
H	15.82969	12.93209	5.100828
C	14.28245	11.69336	4.246922
C	13.54842	12.73598	3.519323
C	13.94902	14.074	3.452038
H	14.84044	14.40574	3.974822
C	13.19891	14.97509	2.697662
H	13.50301	16.01629	2.62785
C	12.05969	14.51571	2.031444
H	11.44507	15.18014	1.430841
C	11.7114	13.17294	2.146163
H	10.83314	12.77019	1.65179
C	14.07445	9.658332	0.964832
H	14.74956	9.710213	1.813113
C	14.53751	9.389568	-0.3208
H	15.59859	9.225396	-0.48673
C	13.61817	9.337429	-1.37141
H	13.94513	9.132212	-2.38752
C	12.26801	9.548023	-1.09523
H	11.53307	9.508565	-1.89365
C	11.86858	9.80994	0.219
C	10.47336	10.03401	0.620804
C	9.386535	9.983857	-0.25705
H	9.544991	9.768173	-1.3092
C	8.097366	10.20121	0.228392
H	7.244856	10.15883	-0.44424
C	7.923908	10.47243	1.587836
H	6.940671	10.65203	2.013334

C	9.043966	10.51418	2.411697
H	8.962316	10.7289	3.472204
N	11.60361	8.374424	3.55252
N	11.00871	10.56746	4.840964
N	13.77075	10.43625	4.122922
N	12.43475	12.30359	2.869838
N	12.7758	9.868748	1.231153
N	10.28837	10.30046	1.944284
O	11.98444	7.351174	2.915958
O	10.8023	11.66708	5.444245
O	8.282133	7.971358	7.958856
Ru	11.9863	10.28837	3.112036

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