

Supporting Information for

**Ruthenium(II) dichloride complexes of chiral,
tetradentate aminosulfoxide ligands:
Stereoisomerism and redox-induced linkage
isomerism**

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Experimental Details

General: Unless otherwise stated, all reactions were performed under a dry nitrogen atmosphere in oven-dried glassware using standard Schlenk techniques, or in a VAC Omni inert atmosphere glove box. Tetrahydrofuran, toluene and diethyl ether solvents were dried using a VAC solvent purification system, whereas hexanes and dichloromethane were distilled from calcium hydride and stored under nitrogen before use. Acetonitrile was dried by storage over activated 4Å molecular sieves under nitrogen. CDCl_3 for NMR spectroscopy was stored over molecular sieves. NMR spectra were obtained using a JEOL ECS-400 MHz spectrometer at room temperature. Chemical shifts are reported in ppm and referenced via residual solvent resonances to Me_4Si (^1H and ^{13}C). In certain cases ^1H and ^{13}C data were assigned using DEPT-135, HETCOR and HMBC experiments. IR spectra were collected on a Nicolet 360 FTIR as KBr disks. Elemental analyses were performed by QTI Intertek, Whitehouse, NJ. (S)-(-)-p-tolyl menthyl sulfinate was supplied by Aldrich, Advanced Asymmetrics, Inc. or synthesized following a literature procedure:¹ commercially supplied material was recrystallized from acetone before use. (R)-p-tolyl vinyl sulfoxide,² (R,R)-N,N'-dimethyl-1,2-cyclohexanediamine,³ $\text{RuCl}_2(\text{PPh}_3)_3$ were synthesized following literature procedures. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and $[\text{NO}]\text{BF}_4$ were supplied by Strem Chemicals Inc.; all other reagents were supplied by Aldrich.

Electrochemistry: Cyclic voltammograms were recorded using a CH Instruments CHI620D electrochemical workstation under nitrogen in a 1-compartment cell using a 3mm diameter glassy-carbon working electrode, a Pt wire auxiliary electrode, and a Ag^+/Ag reference electrode (consisting of a Ag wire in 0.01 M AgNO_3 /0.1M n- Bu_4NPF_6 in CH_3CN solution). All electrodes were supplied by BASi. 0.1 M solutions of n- Bu_4NPF_6 in dry CH_3CN or CH_2Cl_2 were used as the electrolyte and potentials were internally referenced to $\text{Cp}_2\text{Fe}^{+/0}$ by addition of a small amount of Cp_2Fe to the cell at the completion of an experiment.

Thermodynamic and kinetic parameters for the ECEC square scheme were calculated from cyclic voltammograms measured scanning initially in the cathodic direction at various scan rates (0.05 – 3 V/s) following literature methods.^{4, 5} The working electrode was held at 1.2V (vs Ag^+/Ag) for 3 mins before commencing each scan in order to equilibrate the solution in the region around the electrode (see Fig. 4 SI).

UV-vis and CD spectroscopy: UV-vis and CD spectra were recorded in CH_2Cl_2 in 1cm quartz cuvettes at room T on a Varian Cary 50/100 spectrophotometer and Jasco J-815 CD

spectrophotometer respectively. UV-vis spectra of the oxidized complexes (see Fig 5) were measured using an Ocean Optics USB 4000 spectrometer in CH_2Cl_2 /0.1 M $\text{n-Bu}_4\text{NPF}_6$ in a 0.1 cm pathlength quartz spectroelectrochemical cell (BASi) using a Pt grid working electrode, Pt wire auxiliary electrode and the same reference electrode as described above. Spectra were collected every 20 s for 3 minutes while holding the potential constant at 1.2 V (2-L2) or 1 V.

DFT Calculations: Geometries were optimized using density-functional theory with the B97-1 exchange-correlation functional of Hamprecht et al.⁶ with the PQS software package.⁷ Ruthenium was represented by the Hurley et al. relativistic effective core potential (RECP) basis set modified by the Couty-Hall 5p contraction (5311/5311/1111).⁸ Sulfur and chlorine centers used the Wadt-Hay RECP basis set.⁹ Nitrogen and oxygen were represented by Dunning's split-valence triple- ζ basis set.¹⁰ Basis sets for S, Cl, N and O were augmented with a set of polarization and diffuse functions. Hydrocarbon fragments used the double- ζ basis sets of Dunning¹¹ with polarization functions on carbon only. Frequency calculations of the optimized structures were used to confirm the reported structures as minima on the potential energy surface. *Trans* and *cis- α* $\text{RuCl}_2(\text{L1}')$ structures are in good agreement with X-ray structures of **1-L2** and **1-L1**, respectively (Table 3). The lowest energy conformation of *cis- β* isomer (Fig 1) is stabilized by a π -stacking interaction between the sulfoxide Ph groups.

Time-dependent DFT (TD-DFT) calculations of the lowest ten singlet transitions were determined at the B97-1 optimized geometry using Gaussian 09.¹²

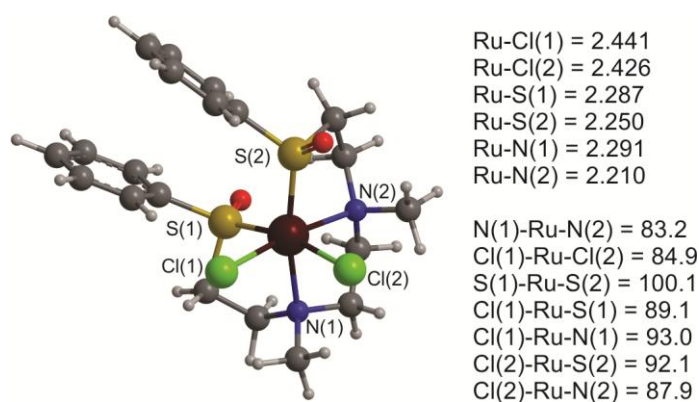


Fig 1. Selected DFT(B97-1) bond distances (Å) and angles (°) for *cis- β* - $\text{RuCl}_2(\text{L1}')$.

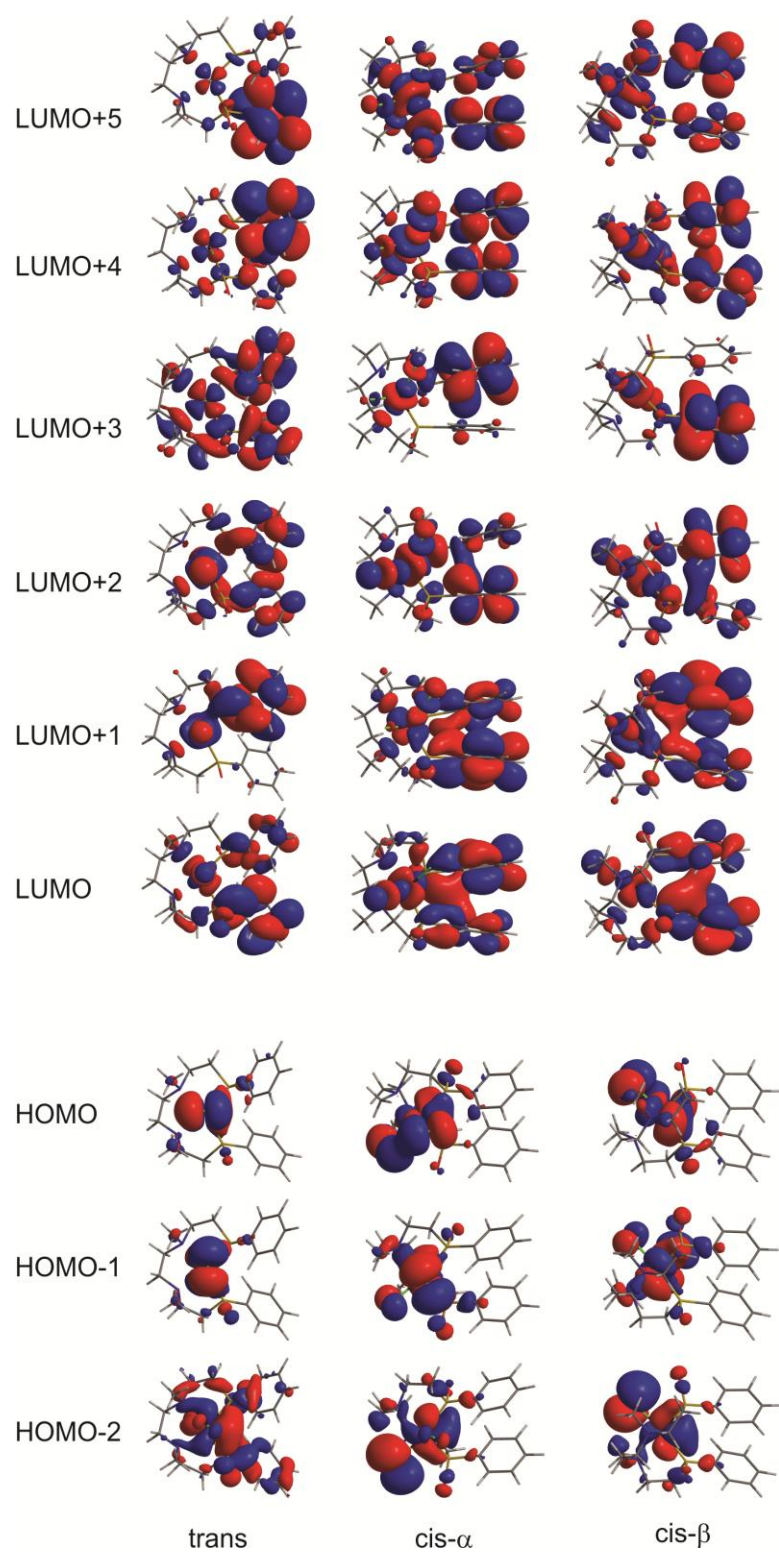


Fig. 2: Isosurfaces of calculated frontier MOs .

(*R_S*, *R_S*)-N,N'-dimethyl-N,N'-di(2-p-tolylsulfinylethyl)-1,2-ethanediamine, (L1)

(*R*)-p-tolyl vinyl sulfoxide (518 mg, 3.12 mmols) and N,N'-dimethylethylenediamine (137 mg, 1.55 mmols) were dissolved in ethanol and refluxed under air for 24 hours. The solvent was removed *in vacuo* and the product recrystallized from ether/hexanes at -20°C. 567 mg (1.35 mmols, 87 %) of a light tan solid was obtained (mp 62-63°C).

Anal. Calcd. for C₂₂H₃₂N₂S₂O₂: C, 62.83; H, 7.68; N, 6.67. Found: C, 65.62; H, 7.54; N, 6.54.

¹H NMR (CDCl₃) δ: 7.52 (d, J=8, 4H, ArH), 7.31 (d, J=8, 4H, ArH), 2.90 (s, 4H, S-CH₂), 2.89 (m, 2H, N-CH₂), 2.57 (m, 2H, N-CH₂), 2.49 (s, 4H, N-CH₂), 2.40 (s, 6H, S-CH₃), 2.25 (s, 6H, N-CH₃)

¹³C{¹H} NMR (CDCl₃) δ: 141.6 (q, Ar), 140.9 (q, Ar), 130.1 (Ar), 124.2 (Ar), 55.5 (S-CH₂), 55.3 (N-CH₂), 50.5 (N-CH₂), 42.5 (N-CH₃), 21.5 (S-CH₃)

IR (KBr disk) cm⁻¹: 3500 (w, broad), 2925 (m), 1595 (w), 1495 (w), 1480 (m), 1445 (m), 1427 (w), 1385 (w), 1170 (m), 1067 (s), 1055 (s), 1025 (m), 945 (m), 930 (m), 870 (w), 810 (m)

[α]_D²⁵ +203.6 (c 1.10, chloroform)

(*R_S*, *R_S*, *R_S*, *R_S*)-N,N'-dimethyl-N,N'-di(2-p-tolylsulfinylethyl)-1,2-cyclohexanediamine, (L2)

(*R*)-p-tolyl vinyl sulfoxide (361 mg, 2.17 mmols) and (*R,R*)-N,N'-dimethyl-1,2-cyclohexanediamine (154 mg, 1.09 mmols) were dissolved in methanol (15 mL) and the solution refluxed under air for 18 hours. The solvent was removed *in vacuo* to give a colorless solid which was recrystallized from CH₂Cl₂/hexanes at -20°C. 183 mg (0.385 mmols, 35.6%) of a colorless crystalline solid was obtained in two crops (mp 174-5 °C).

Anal. Calcd. for C₂₆H₃₈N₂S₂O₂: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.75; H, 7.91; N, 5.93.

¹H NMR (CDCl₃): δ 7.52 (d, J = 8, 4H, ArH), 7.28 (d, J = 8, 4H, ArH), 3.07 (m, 2H), 2.87 (overlapping m, 6H), 2.55 (m, 2H), 2.40 (s, CH₃, 6H), 2.30 (s, CH₃, 6H), 1.74 (m, 4H), 1.22 (m, 2H), 1.19 (m, 2H).

¹³C{¹H} NMR(CDCl₃): δ 141.8, 141.4, 130.1, 124.2, 65.0, 57.8, 48.3, 36.1, 26.5, 25.9, 21.7

IR (KBr disk) cm⁻¹: 3050 (w), 2930 (s), 2860 (m), 2795 (w), 1650 (w), 1595 (w), 1490 (m), 1460 (m), 1400 (w), 1375 (w), 1105 (w), 1085 (m), 1045 (s), 1015 (m), 810 (m)

[α]_D²⁵ +203.2 (c 0.71, chloroform)

Preparation and separation of isomers of RuCl₂(L1): RuCl₂(PPh₃)₃ (536mg, 0.56 mmol) and **L1** (228 mg, 0.56 mmol) were mixed in dry toluene (10 mL) and refluxed under nitrogen for 2 hrs forming a yellow precipitate in a brown solution. The solids were separated by filtration, washed with diethyl ether (5 mL) and dried *in vacuo*, yielding 210 mg, 63 % yield of a yellow powder. ¹H NMR spectroscopy revealed this solid to be a 0.8:1 mixture of a C₂- (**1-L1**) and a C₁-symmetric isomer (**2-L1**). The mixture was heated briefly to 50°C in ethanol (5 mL) and insoluble pink solids filtered off. After removal of solvent *in vacuo*, the pink solid was then crystallized from a concentrated solution in CH₂Cl₂ layered with hexanes to yield pink crystalline material that was analytically pure **1-L1**. Single crystals suitable for X-ray diffraction were grown in the same manner. The yellow ethanol supernatant was evaporated to dryness and the residue dissolved in methylene chloride and filtered and again evaporated to dryness to yield a yellow residue. Microcrystalline material that was pure **2-L1** could be isolated from concentrated solutions in methanol at -20°C.

***cis-α*-RuCl₂(L1), 1-L1 (pink)**

Anal. Calcd. for C₂₂H₃₂N₂S₂O₂RuCl₂: C, 44.58; H, 5.45; N, 4.73. Found: C, 44.36; H, 5.41; N, 4.65.

¹H NMR (CDCl₃) δ: 8.40 (d, 4H, J=8, Ar-H), 7.31 (d, 4H, J=8, Ar-H), 4.41 (m, 2H), 3.41 (m, 6H), 2.99 (s, 6H, N-CH₃), 2.56 (m, 4H), 2.38 (s, 6H, pTol,CH₃)

¹³C NMR (CDCl₃) δ: 142.73 (Ar, quat), 136.86 (Ar, quat), 129.38 (Ar), 128.73 (Ar), 63.33, 60.59, 58.32, 52.81, 21.64 (pTol,CH₃)

IR (KBr Disk) cm⁻¹: 3068 (w), 3037(w), 2981(w), 2923 (w), 2870(w), 2831(w), 1495(w), 1477(w), 1440(w), 1398(w), 1186(w), 1103(m), 1082(s), 1060(s), 1043 (m), 1025 (w), 943(w), 929(w), 818(m), 671 (w), 646(w), 638(w), 628(w), 503(m), 474(s), 444(m)

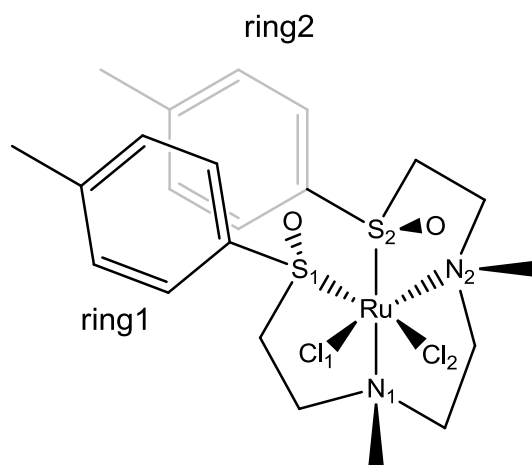
***cis-β*-RuCl₂(L1), 2-L1 (yellow)**

Anal. Calcd. for C₂₂H₃₂N₂S₂O₂RuCl₂: C, 44.58; H, 5.45; N, 4.73. Found: C, 44.07; H, 5.65; N, 4.06.

¹H NMR (CDCl₃) δ: 7.77 (d, 2H, J=9, *o*-Ar2), 7.35 (d, 2H, J=8, *o*-Ar1), 6.82 (d, 2H, J=9, *m*-Ar2), 6.68 (d, 2H, J=8, *m*-Ar1), 4.55 (m, S₁-CHH, 1H), 4.34 (m, S₂-CHH, 1H), 4.11 (m, S₁-CHH and N₁-CHH-CH₂-S₁, 2H), 3.78 (m, N₁-CHH-CHH-N₂, 2H), 3.50 (m, N₂-CHH-CH₂-S₂, 1H), 3.32 (s, 3H, N₂-CH₃), 3.11 (m, S₂-CHH, 1H), 3.01 (m, N₂-CHH-CH₂-N₁,1H), 2.98 (s, 3H, N₁-

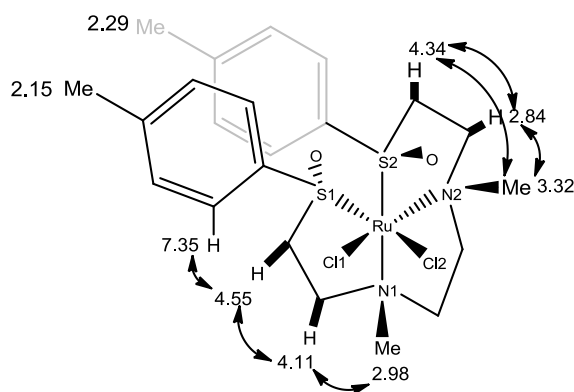
CH₃), 2.84 (m, N₁-CHH-CH₂-S₁ and N₂-CHH-CH₂-S₂, 2H), 2.62 (m, N₂-CH₂-CHH-N₁, 1H), 2.29 (s, 3H, Ar2-CH₃), 2.15 (s, 3H, Ar1-CH₃)

Labeling scheme for assignment of ¹H and ¹³C NMR

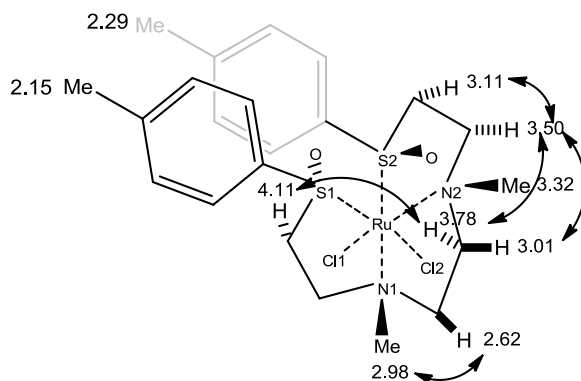


¹³C NMR (CDCl₃) δ: 144.93 (Ar2, S-Cquat), 141.44(Ar2, C-Cquat), 141.26(Ar1, C-Cquat), 139.48(Ar1, S-Cquat), 129.19 (Ar1 *m*-C), 128.87(Ar2 *m*-C), 127.60 (Ar1 *o*-C), 125.06 (Ar2 *o*-C), 69.51 (S₂-CH₂), 65.04 (S₁-CH₂), 64.04 (N₁-CH₂CH₂-N₂), 60.72 (N₁-CH₂CH₂-N₂), 60.67 (N₂-CH₂CH₂-S₂), 55.34 (N₁-CH₂CH₂-S₁), 52.37 (N₂-CH₃), 50.19 (N₁-CH₃), 21.37 (Ar-CH₃), 21.35 (Ar-CH₃)

Solution structure of 2-L1: After complete assignment of the ¹H and ¹³C NMR using a combination of DEPT-135, ¹H-¹H-COSY, HMQC and HMBC experiments, ¹H-¹H NOESY data were collected. Key NOE's used to confirm the structure are shown below. In Fig 2(a) NOEs that establish the aryl ring connectivity and the stereochemistry of N1 (*R*) are shown. In Fig 2(b) NOEs that establish the N2 stereochemistry (*S*) and the ligand wrapping around Ru are shown. These data are fully consistent with the lowest energy DFT calculated isomer, Λ-R_NS_NSS.



(a)



(b)

***trans*-RuCl₂(L1), 3-L1**

Use of RuCl₂(η^4 -1,5cyclooctadiene)(MeCN)₂ as the Ru source, THF or CH₂Cl₂ as solvent, longer reflux times (THF) or room temperature reactions (CH₂Cl₂) lead to more complex mixtures of isomers, however **1-L1** and **2-L1** were always observed as the dominant species. In certain cases very small amounts (< 3mg) of an orange isomer, **3-L1**, were also isolated: This is assigned to be the *trans*-isomer due to the similarity of its ¹H NMR spectrum in the aromatic region to that of **1-L2**.

¹H NMR (CDCl₃) δ : 8.26 (d, 2H, J=9, Ar), 7.80 (d, 2H, J=8, Ar), 7.24 (d, 2H, J=8, ArH), 7.22 (d, 2H, J=8, ArH), 5.05(app q, 1H), 4.53 (m, 2H), 4.29 (m, 2H), 4.10 (m, 1H), 3.72 (m, 1H), 3.47 (m, 2H), 3.22 (s, 3H, N-CH₃), 3.01 (m, 2H), 2.90 (m, 1H), 2.77 (s, 3H N-CH₃), 2.32 (s, 3H Ar-CH₃), 2.31(s, 3H Ar-CH₃)

Preparation and separation of isomers of RuCl₂(L2): RuCl₂(PPh₃)₃ (277 mg, 0.289 mmol) and L2 (135 mg, 0.285 mmol) were mixed in dry THF (15 mL) and refluxed under nitrogen for 24 hrs forming a yellow precipitate. The solids were separated by filtration, washed with diethyl ether (5 mL) and dried *in vacuo*, yielding 112mg (61 % yield) of a yellow powder. ¹H NMR spectroscopy revealed this solid to be a 1:1 mixture of two C₁-symmetric isomers (**1-L2** and **2-L2**). These were separated by addition of a small volume of acetonitrile: **2-L2** rapidly dissolved to form a yellow solution which was quickly separated from the remaining orange microcrystalline material (**1-L2**) by filtration. **1-L2** was recrystallized by layering a concentrated CH₂Cl₂ solution with hexane, to yield single crystals suitable for single crystal X-ray diffraction. The acetonitrile solution containing primarily **2-L2** was evaporated to dryness to give a yellow

residue. Addition of methanol to this residue gave a bright lemon-yellow powdery solid that was pure **2-L2** by ^1H NMR. **2-L2** could also be recrystallized from concentrated chloroform solutions at -20°C to give a very fine yellow powdery solid.

***trans*-RuCl₂(L2), 1-L2 (orange)**

Anal. Calcd. for C₂₆H₃₈N₂S₂O₂RuCl₂: C, 48.28; H, 5.93; N, 4.33. Found: C, 48.49; H, 5.99; N, 4.25.

^1H NMR (CDCl₃): δ 8.29 (d, J=8, 2H, ArH), 7.70 (d, J=8, 2H, Ar-H), 7.24 (d, J=8, 2H, Ar-H), 7.19 (d, J=8, 2H, Ar-H), 4.96 (t of d, J=11, 4, 1H), 4.62 (q, J=10, 1H), 4.45 (m, 2H), 4.33 (t of d, J=14, 4, 1H), 4.16-4.05 (m, 2H), 3.25 (s, 3H, NCH₃), 3.23 (m, 1H), 3.08 (d of d, J=12, 3, 1H), 2.82 (m, 1H), 2.69 (s, 3H, N-CH₃), 2.34 (s, 3H, ArCH₃), 2.31 (s, 3H, ArCH₃), 2.29 (m, 1H), 2.12 (br d, 1H), 1.91 (br d, 1H), 1.82 (br d, 1H), 1.73 (d of d, 1H), 1.61 (m, 1H), 1.51 (m, 1H), 1.35 (m, 1H)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃) δ : 144.98 (quat, Ar), 144.24 (quat, Ar), 142.05 (quat, Ar), 141.12 (quat, Ar), 129.24 (Ar), 129.21 (Ar), 127.07 (Ar), 126.89 (Ar), 76.24, 71.68, 69.61, 64.56, 54.43, 54.33, 52.39, 41.52, 26.73, 26.13, 26.12, 24.45, 21.53, 21.52

IR (KBr Disk) cm⁻¹: 3057 (w), 3023 (w), 2969 (w), 2932 (s), 2863 (m), 1491 (w), 1448 (m), 1422 (w), 1396 (m), 1094 (s), 1076 (s), 1063 (s), 1025 (w), 973 (w), 915 (w), 885 (w), 877 (w), 808 (m), 754 9w), 708 (w), 648 (m), 631 (m), 537 (m), 512 (m), 495 (m), 482 (m), 440 (m), 415 (m)

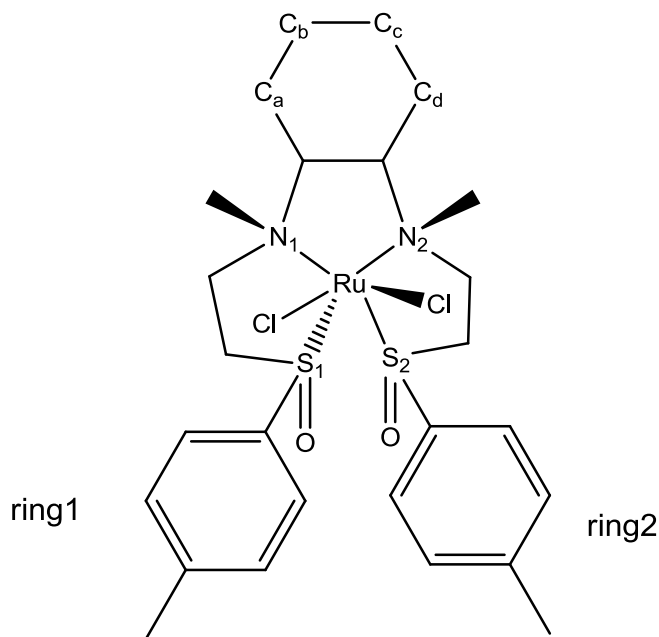
***cis*- β -RuCl₂(L2), 2-L2 (yellow)**

Anal. Calcd. for C₂₆H₃₈N₂S₂O₂RuCl₂: C, 48.28; H, 5.93; N, 4.33. Found: C, 47.82; H, 5.93; N, 4.12.

^1H NMR (CDCl₃) δ : 7.56 (d, J=8, 2H, *o*-Ar2), 7.39 (d, J=8, 2H, *o*-Ar1), 6.97 (d, J=8, 2H, *m*-Ar2), 6.80 (d, J=8, 2H, *m*-Ar1), 5.15 (t of d J=13,5, 1H, N₂-CHH), 4.70 (t of d, J=11,4, 1H, N₂-CH), 4.52 (m, 1H, S₁-CHH), 4.12 (t of 6, J=14,5, 1H, S₂-CHH), 4.00 (d of d, J=15,5, 1H, S₂-CHH), 3.54 (m, 1H, N₁-CHH), 3.41 (s, 3H, N₁-CH₃), 3.35 (m, 1H, S₁-CHH), 3.24 (m, 1H, N₁-CH), 3.22 (m, 1H, N₁-CHH), 2.76 (s, 3H, N₂-CH₃), 2.63 (d of d, J=12, 5, 1H, N₂-CHH), 2.26 (s, 3H, Ar2-CH₃), 2.25 (s, 3H, Ar1-CH₃), 2.19 (m, 1H, C_aHH), 2.05 (m, 1H, C_dHH), 1.92 (m, 1H, C_aHH), 1.90 (m, 1H, C_bHH), 1.78 (m, 1H, C_cHH), 1.41 (m, 1H, C_dHH), 1.29 (m, 1H, C_cHH), 1.17 (m, 1H, C_bHH)

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 144.26 (Ar2 S-Cquat), 141.57(Ar2 C-Cquat), 141.21(Ar1 C-Cquat), 139.92(Ar2 S-Cquat), 129.33 (Ar2 *m*-C), 128.39 (Ar1 *m*-C), 127.35 (Ar1 *o*-C), 125.90 (Ar2 *o*-C), 75.03 ($\text{N}_1\text{-CH}$), 69.49 ($\text{N}_2\text{-CH}$), 68.27 ($\text{S}_2\text{-CH}_2$), 65.30 ($\text{S}_1\text{-CH}_2$), 60.73 ($\text{N}_1\text{-CH}_2$), 57.91 ($\text{N}_2\text{-CH}_2$), 47.55 ($\text{N}_2\text{-CH}_3$), 46.41 ($\text{N}_1\text{-CH}_3$), 26.95 (C_a), 25.44 (C_b), 25.13 (C_d), 23.86 (C_c), 21.30 (Ar2-CH_3), 21.23 (Ar1-CH_3)

Labeling scheme for assignment of ^1H and ^{13}C NMR



IR (KBr Disk) cm^{-1} : 3057 (w), 3022 (w), 2932 (s), 2862 (m), 1491 (w), 1448 (w), 1396 (m) 1095 (s), 1076 (s), 1063 (s), 848 (m), 808 (m), 648 (w), 634 (w), 537 (m), 514 (m)

Bulk oxidation of 2-L2: 2-L2 (16 mg, 2.5×10^{-5} mols) and $[\text{NO}]^+[\text{BF}_4]^-$ (3 mg, 1 eq) were stirred in dry CH_2Cl_2 under nitrogen for 20 mins, during which time the solution turned from yellow to dark orange. Addition of excess hexane (6 mL) dropwise precipitated an orange solid, which was isolated and dried *in vacuo*.

Selected IR data (solid, ATR method) cm^{-1} : 1091(s), 1063 (vs, BF_4), 924 (m), 806 (s)

Fig 3a: UV-vis spectra of $\text{RuCl}_2(\text{L})$ complexes

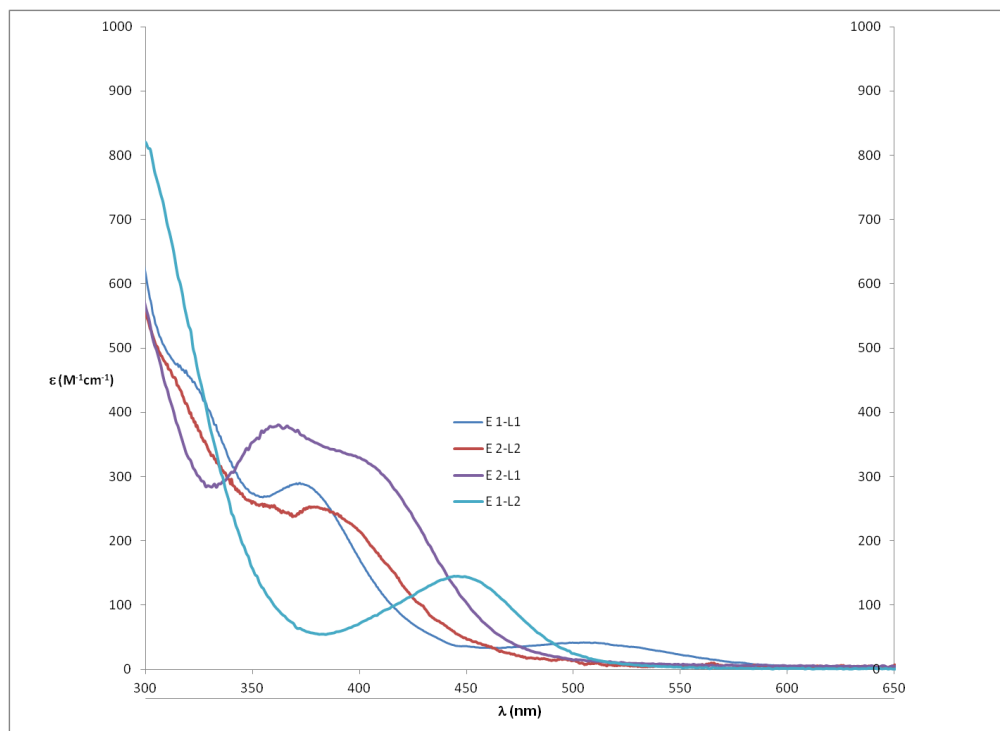


Fig 3b: CD spectra of $\text{RuCl}_2(\text{L})$ complexes

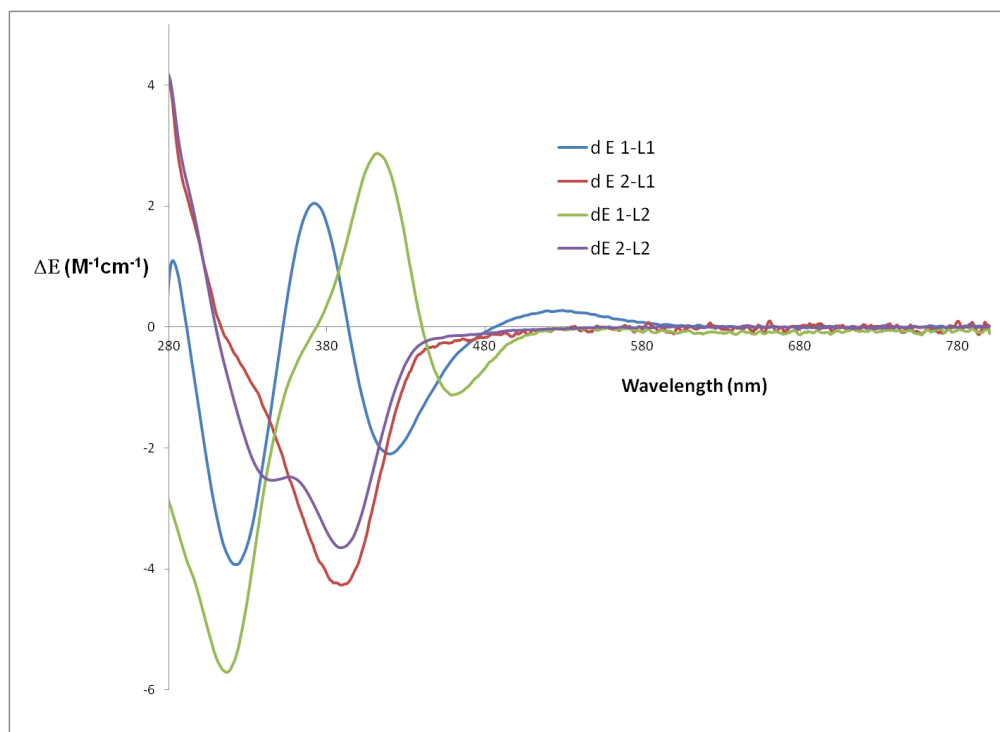


Fig 4: Cyclic voltammograms of **2-L2** at various scan rates with initial cathodic scanning direction after preconditioning the solution at 1.2 V for 180s.

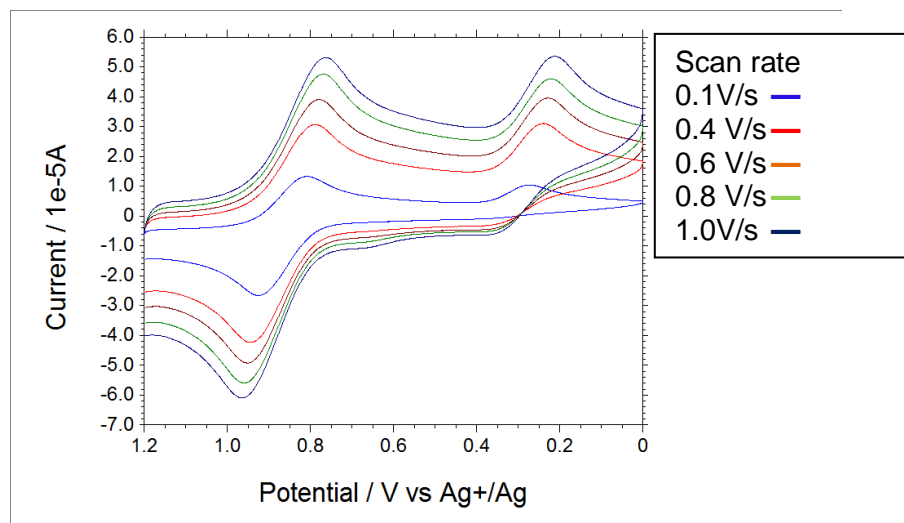
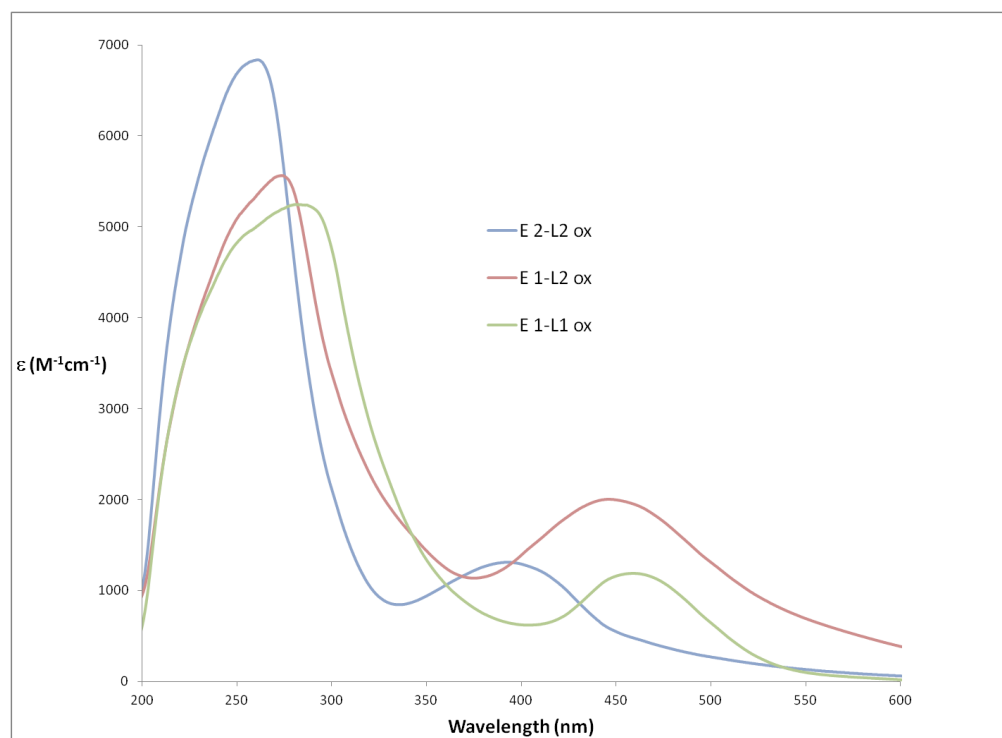


Fig 5: UV-vis of oxidized Ru complexes obtained in a spectroelectrochemical cell after oxidation for 3 mins in CH_2Cl_2 / 0.1 M TBA.PF₆



X-ray Data Collection, Structure Determination and Refinement

Table 1: Crystal data and structure refinement for 1-L2, *trans*-RuCl₂(L2).

Empirical formula	C ₂₆ H ₃₈ Cl ₂ N ₂ O ₂ Ru S ₂	
Formula weight	646.67	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C ₂	
Unit cell dimensions	a = 24.559(2) Å	α = 90°
	b = 9.5482(9) Å	β = 102.5570(10)°
	c = 11.6554(11) Å	γ = 90°
Volume	2667.7(4) Å ³	
Z	4	
Density (calculated)	1.610 g/cm ³	
Absorption coefficient	0.973 mm ⁻¹	
F(000)	1336	
Crystal size	0.30 x 0.22 x 0.16 mm ³	
Crystal color, habit	Orange rod	
Theta range for data collection	1.79 to 25.68°	
Index ranges	-29 ≤ h ≤ 28, -11 ≤ k ≤ 11, -13 ≤ l ≤ 14	
Reflections collected	11776	
Independent reflections	4772 [R(int) = 0.0281]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8599 and 0.7590	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4772 / 1 / 317	
Goodness-of-fit on F ²	1.016	
Final R indices [I > 2σ(I)]	R1 = 0.0199, wR2 = 0.0507	
R indices (all data)	R1 = 0.0205, wR2 = 0.0512	
Absolute structure parameter	-0.017(17)	
Extinction coefficient	0.00118(12)	
Largest diff. peak and hole	0.491 and -0.395 e Å ⁻³	

Table 2. Crystal data and structure refinement for 1-L1, cis- α -RuCl₂(L1).

Empirical formula	C ₂₂ H ₃₂ Cl ₂ N ₂ O ₂ Ru S ₂	
Formula weight	592.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.7705(6) Å	$\alpha = 90^\circ$
	b = 12.8827(7) Å	$\beta = 90^\circ$
	c = 14.5232(7) Å	$\gamma = 90^\circ$
Volume	2389.3(2) Å ³	
Z	4	
Density (calculated)	1.647 g/cm ³	
Absorption coefficient	1.078 mm ⁻¹	
F(000)	1216	
Crystal size	0.32 x 0.12 x 0.08 mm ³	
Crystal color, habit	Orange rod	
Theta range for data collection	2.11 to 25.42°	
Index ranges	-11 ≤ h ≤ 15, -15 ≤ k ≤ 14, -17 ≤ l ≤ 17	
Reflections collected	10552	
Independent reflections	4387 [R(int) = 0.0340]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9187 and 0.7243	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4387 / 0 / 284	
Goodness-of-fit on F ²	1.107	
Final R indices [I > 2σ(I)]	R1 = 0.0357, wR2 = 0.0796	
R indices (all data)	R1 = 0.0388, wR2 = 0.0811	
Absolute structure parameter	0.00(4)	
Largest diff. peak and hole	1.057 and -0.547 e Å ⁻³	

Table 3: Important bond lengths and angles for 1-L2 and 1-L1 and comparison to DFT calculated values.

	<i>trans</i> -RuCl ₂ (L ₂), 1-L2 (X-ray)	<i>trans</i> -RuCl ₂ (L ₁ '), DFT(B97-1)	<i>cis</i> - α -RuCl ₂ (L ₁), 1-L1 (X-ray)	<i>cis</i> - α -RuCl ₂ (L ₁ '), DFT(B97-1)
Ru(1)-N(1)	2.164(2)	2.215	2.186(4)	2.230
Ru(1)-N(2)	2.175(2)	2.215	2.198(4)	2.231
Ru(1)-S(1)	2.2208(6)	2.250	2.2726(13)	2.303
Ru(1)-S(2)	2.2482(6)	2.269	2.2834(13)	2.304
Ru(1)-Cl(2)	2.3939(5)	2.436	2.4189(12)	2.446
Ru(1)-Cl(1)	2.4502(5)	2.513	2.4328(12)	2.450
S(1)-O(1)	1.4824(17)	1.530	1.486(3)	1.543
S(2)-O(2)	1.4791(18)	1.528	1.494(3)	1.543
N(1)-Ru(1)-N(2)	83.20(8)	83.0	83.36(15)	84.0
N(1)-Ru(1)-S(1)	82.88(6)	82.3	81.92(12)	82.4
N(2)-Ru(1)-S(2)	86.49(6)	87.8	81.86(11)	82.4
S(1)-Ru(1)-S(2)	107.25(3)	106.7	178.69(5)	177.2
Cl(2)-Ru(1)-Cl(1)	178.91(2)	176.1	95.10(4)	92.9
N(2)-Ru(1)-Cl(1)	88.50(5)	87.8	90.60(11)	92.2
N(1)-Ru(1)-Cl(2)	93.58(5)	91.1	92.22(12)	91.8

References

1. M. Hulce, J. P. Mallomo, L. L. Frye, T. P. Kogan and G. Posner, *Org. Synth.*, 1990, **Coll. Vol. 7**, 495.
2. B. Ronan and H. B. Kagan, *Tetrahedron: Asymmetry*, 1992, **3**, 115-122.
3. A. Alexakis, S. Mutti and P. Mangeney, *J. Org. Chem.*, 1992, **57**, 1224-1237.
4. D. O. Silva and H. E. Toma, *Can. J. Chem.*, 1994, **72**, 1705-1708.
5. R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706-723.
6. Hamprecht, F.A.; Cohen, A.; Tozer, D.J.; Handy, N.C. *J. Chem. Phys.* **1998**, *109*, 6264-6271.
7. PQS version 3.3, Parallel Quantum Solutions, Fayetteville, AR, 2007.
8. (a) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812-2824. (b) Couty, M.; Hall, M.B. *J. Comput. Chem.* **1996**, *17*, 1359-1370.
9. Wadt, W.R., Hay, P.J. *J. Chem. Phys.* **1985**, *82*, 284-298.
10. Dunning, T.H. *J. Chem. Phys.* **1971**, *55*, 716-723.
11. Dunning, T.H.; Hay, P.J. in *Modern Theoretical Chemistry*. ed. H.F. Schaefer. vol 3, Plenum, New York, 1976.

12. Gaussian 09, Revision B.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.