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Ruthenium(II) 2,2′-bipyridine complexes incorporating substituted phenylazo-(2-(phenylthio))phenylmethine ancillary ligands. Synthesis, crystal structure, spectroscopic and redox properties

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Abstract Five ruthenium complexes bearing phenylazo-(2-(phenylthio))phenylmethine ligands of the general type *trans*-[$\mathrm{Ru^{II}(bpy)(L)(Cl)_2}$] (*C1–C5*) {L = $\mathrm{YC_6H_4N{=}NC(COCH_3){=}NC_6H_4(2\text{-}SC_6H_5)}$, H (*L1*), Cl (*L2*), $\mathrm{OCH_3}$ (*L3*), Br (*L4*), or $\mathrm{NO_2}$ (*L5*)} have been synthesized. The crystal structure of *trans*-[Ru(bpy)(*L1*)$\mathrm{(Cl)_2}$] (*C1*) is reported and shows no direct metal–S interaction. The complexes have been characterized through spectroscopic (IR, UV/vis and NMR) and electrochemical (CV) techniques. The electrochemical parameters (E_L(L)) of the azoimine ligands are reported.

Introduction

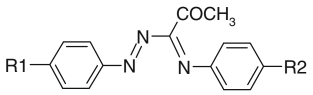
Late transition metal complexes with α-diimine ligands bearing ortho-alkoxy or thiophenyl groups exhibit a good catalytic ability toward olefin polymerization reactions [1–4]. For example, titanium(IV) complexes containing monoanionic phenoxy modified salicylaldiminate ligands have been prepared and found to exhibit high catalytic activity for ethylene polymerization and also copolymerization of ethylene with 1-hexene in the presence of modified methylaluminoxane [5].

We are interested in the synthesis and complexation of azoimine ligands (Scheme 1). The electronic properties of such ligands can be tuned easily by changing the R1 and R2 substituents, which influence both the coordination ability of these ligands and the electronic properties of their complexes [6–9].

In this report, a family of substituted phenylazo-(2-(phenylthio))phenylmethine ligands have been prepared, characterized and coordinated to Ru(II). The effects of these ligands on the electronic properties and structures of the Ru(II) complexes are reported.

Experimental

Aniline derivatives, α-chloroacetylacetone, 2-thiophenylaniline, ruthenium trichloride hydrate, 2,2′-bipyirdine, lithium chloride and solvents (reagent grade) were purchased from Aldrich and used as received. Tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice from 1:1 ethanol/water and vacuum dried at 110 °C. Hydrazonyl chlorides were prepared according to reported procedures [10].



Scheme 1

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General preparation of the azoimine ligands (L)

A solution of 2-thiophenylaniline (1.86 g, 20 mmol), triethylamine (2.4 g, 24 mmol) and the appropriate hydrazonyl chloride (20 mmol) in 15.0 cm^3 ethanol was refluxed for 2 h. Cooling the solution produced a yellow solid that was recrystallized from ethanol.

1-(Phenylhydrazono)-1-{[2-(phenylthio) phenyl]imino}acetone (*L1*)

Yield = 4.05 g, 56%. M.p = 107–109 °C. I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}496$, $\nu_{C=N} = 1{,}601$, $\nu_{C=O} = 1{,}668$. ^1H NMR ($CDCl_3$): δ 7.55 (d, 1H,H5), 7.30 (d, 2H, H1, H3), 7.20 (m, 6H, H7, H9, H10, H11, H12, H13), 7.00 (d, 2H, H2, H4), 6.95 (t, 1H, H6), 6.91 (t, 1H, HY), 6.25 (d, 1H, H8), 2.55 (s, 3H, $COCH_3$). UV.–Vis. in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 352 (8.83×10^4), 294 (5.24×10^4), 214 (6.90×10^4). $C_{21}H_{17}N_3OS$, Found. C, 70.4; H, 5.0; N, 11.4%. Calculated: C, 70.2; H, 4.8; N, 11.7%.

1-(4-Chlorophenylhydrazono)-1-{[2-(phenylthio) phenyl]imino}acetone (*L2*)

Yield = 4.1 g, 52%. M.p = 132–134 °C. I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}478$, $\nu_{C=N} = 1{,}599$, $\nu_{C=O} = 1{,}664$. ^1H NMR (in $CDCl_3$): δ 7.50 (d, 1H, H5), 7.30 (m, 6H, H6, H9, H10, H11, H12, H13), 7.19 (d, 2H, H1, H3), 7.05 (1H, t, H7), 6.95 (2H, d, H2, H4), 6.22 (d, 1H, H8), 2.55 (s, 3H, $COCH_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 353 (8.09×10^4), 294 (4.69×10^4), 240 (6.24×10^4). $C_{21}H_{16}N_3ClOS$, Found: C, 64.1; H, 4.2; N, 10.5%. Calculated: C, 64.0; H, 4.1; N, 10.7%.

1-(4-Methoxyphenylhydrazono)-1-{[2-(phenylthio) phenyl]imino}acetone (*L3*)

Yield = 4.7 g, 60%. M.p. = 105–107 °C I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}491$, $\nu_{C=N} = 1{,}599$, $\nu_{C=O} = 1{,}675$. ^1H NMR ($CDCl_3$) δ: 7.52 (d, 1H, H5), 7.25 (m, 6H, H7, H9, H10, H11, H12, H13), 7.05 (d, 2H, H1, H3) 6.90 (t, 1H, H6), 6.85 (d, 2H, H2, H4), 6.23 (d, 1H, H8), 3.8 (s, 3H, OCH3), 2.55 (s, 3H, $COCH_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 351 (9.01×10^4), 297 (5.38×10^4), 245 (7.02×10^4). $C_{22}H_{19}N_3O_2S$, Found: C, 67.7; H, 4.8; N, 10.5%. Calculated: C, 67.8; H, 4.9; N, 10.8%.

1-(4-bromophenylhydrazono)-1-{[2-(phenylthio) phenyl]imino}acetone(*L4*)

Yield = 4.5 g, 51%. M.p. = 123–127 °C. I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}478$, $\nu_{C=N} = 1{,}596$, $\nu_{C=O}$ 1,675. ^1H NMR ($CDCl_3$): δ 7.50 (d, 1H, H5), 7.35 (d, 2H, H1, H3), 7.15 (m, 6H, H7, H9, H10, H11, H12, H13), 6.95 (t, 1H, H6), 6.80 (d, 2H, H2, H4), 6.22 (d, 1H, H8), 2.50 (s, 3H, $COCH_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 351 (8.92×10^4), 294 (5.32×10^4), 243 (6.98×10^4). $C_{21}H_{16}BrN_3OS$, Found: C, 57.5; H, 3.8; N, 9.4%. Calculated: C, 57.5; H, 3.7; N, 9.6%.

1-(4-Nitrophenylhydrazono)-1-{[2-(phenylthio) phenyl]imino}acetone (*L5*)

Yield = 4.0 g, 49%. M.p. = 148–150 °C. I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}500$, $\nu_{C=N} = 1{,}605$, $\nu_{C=O} = 1{,}673$. ^1H NMR ($CDCl_3$,): δ 8.15 (d, 2H, H1, H3), 7.50 (d, 1H, H5), 7.20 (d, 2H, H2, H4), 7.05 (m, 6H, H7, H9, H10, H11, H12, H13), 6.85 (t, 1H, H6), 6.22 (d, 1H, H8), 2.50 (s, 3H, $COCH_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 358 (8.80×10^4), 294 (5.20×10^4), 210 (6.86×10^4). $C_{21}H_{16}N_4O_3S$, Found: C, 62.5; H, 3.7; N, 13.7%. Calculated: C, 62.4; H, 4.0; N, 13.8.

Preparation of trans-[Ru(bipy)(L)Cl_2]; general procedure

$RuCl_3.3H_2O$ (0.26 g, 1.0 mmol) and (1.0 mmol) of (*L*) were dissolved in absolute ethanol (100 cm^3). After refluxing for 1 h, bipy (1.0 mmol) was added and the reaction was heated under reflux for an additional 3 h and then an excess of LiCl (0.50 g, 11.8 mmol) was added. After allowing the reaction mixture to reflux for an additional 1 h, the solvent was removed by rotary evaporator. The crude product was dissolved in dichloromethane (20 cm^3) and purified by column chromatography (50 × 3 cm) containing 250 g of grade (III) alumina. The first pale yellow band of the azomethine ligand (*L*) was eluted with hexane. Acetone was used to elute the second dark-red band of the product.

*trans-[Ru(*bipy*)(L1)(Cl)$_2$] (C1)*

Yield = 0.32 g, 52%. I.r. (KBr, cm^{-1}): $\nu_{N=N} = 1{,}485$, $\nu_{C=N} = 1{,}616$, $\nu_{C=O} = 1701$. ^1H NMR ($CDCl_3$) δ 8.11 (d, 2H, H1, H3), 7.98 (d, 1H, H14), 7.9 (d, 1H, H21), 7.88 (d, 1H, H17), 7.81 (d, 1H, H18), 7.78 (d, 1H, H5), 7.70 (t, 1H, H19), 7.67 (d, 2H, H2, H4), 7.5 (d, 2H, H5, H8), 7.40 (d, 1H, H7), 7.06 (m, 7H, H6, H9, H10, H11, H12, H13, H20), 6.90 (t,1H, H15), 6.70 (t, 1H, H16), 2.76 (s, 3H, $COCH_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 510 (6.870×10^3), 374 (8.710×10^3), 285 (2.979×10^4). $C_{31}H_{25}N_5OSRuCl_2 \cdot 0.5\ H_2O$, Found: C, 53.5%; H, 3.8; N, 10.2%. Calculated: C, 53.2; H, 3.7; N, 10.0%.

trans-[Ru(bipy)(*L2*)Cl$_2$] (*C2*)

Yield = 0.33 g, 45%. I.r. (KBr, cm^{-1}): IR: $\nu_{N=N}$ = 1,486, $\nu_{C=N}$ = 1,616, $\nu_{C=O}$ = 1,717 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.13 (d, 2H, H1, H3), 7.97 (d, 1H, H14), 7.93 (d, 1H, H21), 7.90 (d, 1H, H5), 7.87 (t, 1H, H15), 7.79 (t, 1H, H20), 7.45 (d, 2H, H2, H4), 7.40 (t, 1H, H16), 7.36 (d, 1H, H19), 7.30 (d, 1H, H8), 7.10 (t, 1H, H7), 7.15 (m, 7H, H9, H10, H11, H12, H13, H17, H18), 7.05 (t, 1H, H6), 2.86 (s, 3H, COCH$_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 512 (6.66 × 10^3), 351 (8.710 × 10^3), 281 (2.887 × 10^4). $C_{31}H_{24}N_5OSRuCl_2$, Found: C, 51.4; H, 3.2; N, 9.4%. Calculated: C, 51.5; H, 3.3; N, 9.7.

trans-[Ru(bipy)(*L3*)(Cl)$_2$] (*C3*)

Yield = 0.31 g, 43%. I.r. (KBr, cm^{-1}): $\nu_{N=N}$ = 1,490, $\nu_{C=N}$ = 1612, $\nu_{C=O}$ = 1,705. ^{1}H NMR (CDCl$_3$): δ 8.18 (d, 2H, H1, H3), 8.07 (d, 1H, H14), 7.91 (d, 1H, 21), 7.87 (d, 1H, H5), 7.81 (t, 1H, H15), 7.77 (t, 1H, H20), 7.42 (d, 2H, H2, H4), 7.30 (m, 8H, H9, H10, H11, H12, H13, H17, H18, H19), 7.20 (t, 1H, H16), 7.12 (d, 1H, H8), 7.08 (t, 1H, H6), 6.95 (t,1H, H7), 3.91 (s, 3H, OCH$_3$), 2.86 (s, 3H,COCH$_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 516 (6.70 × 10^3), 378 (8.50 × 10^3), 284 (2.905 × 10^4). $C_{32}H_{27}N_5O_2SRuCl_2$, Found: C, 53.3; H, 3.6; N, 9.5%. Calculated: C, 53.6; H, 3.8; N, 9.7%.

trans-[Ru(bipy)(*L4*)(Cl)$_2$] (*C4*)

Yield = 0.38 g, 47%. I.r. (KBr, cm^{-1}): $\nu_{N=N}$ = 1,480, $\nu_{C=N}$ = 1,611, $\nu_{C=O}$ = 1,701. ^{1}H NMR (CDCl$_3$): δ 8.05 (d, 2H, H1, H3), 7.98 (d, 1H, H14), 7.95 (d, 1H, H21), 7.90 (d, 1H, H5), 7.88 (t, 1H, H15), 7.81 (t, 1H, H20), 7.77 (d, 1H, H18), 7.62 (d, 2H, H2, H4), 7.41 (d, 1H, H17), 7.20 (d, 1H, H8), 7.15 (t, 1H, H7), 7.11 (t, 1H, H19), 7.06 (t, 1H, H16), 6.90 (m, 6H, H6, H9, H10, H11, H12, H13), 2.78 (s, 3H, COCH$_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 510 (6.69 × 10^3), 374 (8.52 × 10^3), 281 (2.90 × 10^4). $C_{31}H_{24}N_5OSRuBrCl_2 \cdot 0.5\ CH_2Cl_2$, Found: C, 46.5; H, 3.3; N, 8.4%. Calculated: C, 46.8; H, 3.1; N, 8.7%.

trans-[Ru(bipy)(*L5*)Cl$_2$]•CH$_2$Cl$_2$ (*C5*)

Yield = 0.33 g, 40%. I.r. (KBr, cm^{-1}): $\nu_{N=N}$ = 1,495, $\nu_{C=N}$ = 1,606, $\nu_{C=O}$ = 1,711. ^{1}H NMR (CDCl$_3$): δ 8.48 (d, 2H, H1, H3), 8.41 (d, 1H, H21), 8.38 (d, 1H, H14), 7.98 (d, 1H, H5), 7.96 (d, 1H, H17), 7.94 (d, 1H, H18),7.90 (t, 1H, H16), 7.82 (t, 1H, H19), 7.40 (d, 2H, H2, H4), 7.30 (d, 1H, H8), 7.20 (m, 7H, H9, H10, H11, H12, H15, H13, H20), 7.00 (t, 1H, H7), 6.90 (t, 1H, H6), 2.79 (s, 3H, COCH$_3$). UV–Vis in acetonitrile: λ_{max}(nm) (ε_{max}, M^{-1} cm^{-1}): 510 nm (6.71 × 10^3), 370 (8.58 × 10^3), 287 (2.91 × 10^4). $C_{31}H_{24}N_6O_3SRuCl_2 \cdot CH_2Cl_2$, Found: C, 46.8; H, 3.5; N, 10.4%. Calculated: C, 47.0; H, 3.2; N, 10.3%.

Instrumentation

Microanalyses (C, H, N) were performed using an elemental analyzer EURO VECTOR model EA3000. IR spectra were obtained with an FT-IR JASCO model 420. Electronic spectra were recorded on a Shimadzu 240 UV–visible spectrophotometer. The ^{1}H spectra were measured on a Bruker-Avance 400-MHz spectrometer at 400 MHz using TMS as an internal standard. Electrochemical measurements were performed in 99.8% anhydrous acetonitrile (Aldrich, HPLC grade) using a Volta Lab model PGP201 instrument with a platinum working electrode (1.6 mm diameter), a platinum wire auxiliary electrode and silver wire pseudo-reference electrode. Ferrocene (0.665 V versus NHE) is used as an internal reference [11]. To control the temperature, a Haake D8-G refrigerated bath and circulator were used to maintain the cell temperature at 25.0 ± 0.1 °C. Tetrabutylammonium hexafluorophosphate (0.1 M) was twice recrystallized and vacuum dried at 110 °C and used as the supporting electrolyte.

Crystallography

A suitable crystal of compound C1 was selected, attached to a glass fiber and data were collected at 298(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) [12]. Data were measured using omega scans 0.3° per frame for 10 s, and a full sphere of data was collected. A total of 2,400 frames were collected with a final resolution of 0.77 Å. Cell parameters were retrieved using SMART software and refined using SAINTPlus on all observed reflections [13]. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [14]. The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package [15]. The number of reflections used to determine the unit cell was 7,134, and they were between θ_{min} of 1.65 and θ_{max} of 27.50°. The space group was determined to be $P2(1)/n$ by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in constrained positions and assigned isotropic thermal parameters of 1.2 times the riding atoms. The phenyl ring attached to the S atom was disordered and could be modeled in two positions with partial occupancy (45:55%) but without improvement in the R-factors. The structure reported here is for the atoms of the phenyl ring in one average position with large displacement parameters. No decomposition was

Table 1 Crystal data and structure refinement for complex (*C1*)

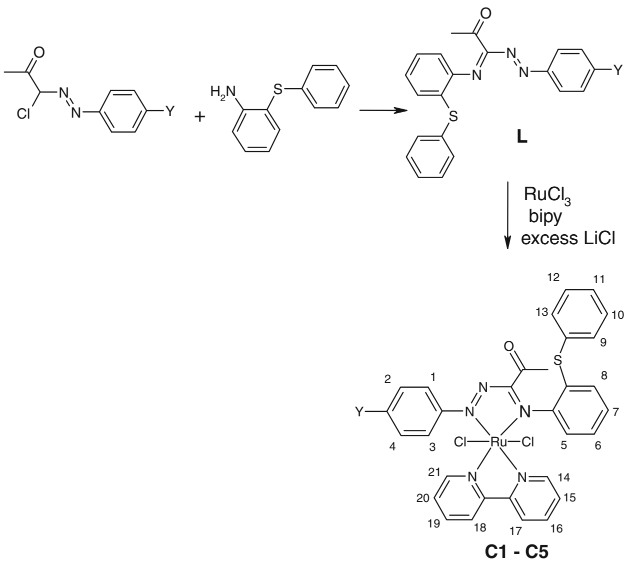
Empirical formula	C_{31} H_{25} Cl_2 N_5 O Ru S
Formula weight	687.59
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
Unit cell dimensions	*a* (Å) = 8.7585(3) α (°) = 90.
	b (Å) = 24.8033(9) Å (*β*°) = 104.1470(10)°
	c (Å) = 14.6855(5) γ (°) = 90.
V ($Å^3$)	3093.52(19)
Z	4
Density (calculated)	1.476 Mg/m^3
Absorption coefficient	0.780 mm^{-1}
F(000)	1,392
Crystal size	0.25 × 0.19 × 0.08 mm^3
Theta range for data collection	1.65 to 27.50°.
Index ranges	$-11 \leq h \leq 11$
	$-32 \leq k \leq 32$
	$-19 \leq l \leq 19$
Reflections collected	45,547
Independent reflections	7,113 [*R*(int) = 0.0550]
Completeness to theta = 27.50°	100.0%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7,113/0/366
Goodness-of-fit on F^2	1.041
Final *R* indices [$I > 2$sigma(I)]	$R1 = 0.0412$, $wR2 = 0.0869$
R indices (all data)	$R1 = 0.0616$, $wR2 = 0.0964$
Largest diff. peak, hole ($eÅ^{-3}$)	0.690 and −0.332 $eÅ^{-3}$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

observed during data collection. Details of the data collection and refinement are given in Table 1. Further details, including a drawing showing the disordered phenyl group over two positions, are provided in the Supporting Information. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 755584 & 755585.

Results and discussion

Five substituted phenylazo-(2-(phenylthio))phenylmethine ligands (*L1–L5*) bearing different substituents (Y) were synthesized by condensation of the corresponding hydrazonyl chloride with (2-(phenylthio)aniline in high yields (Scheme 2). Pure products were obtained as yellow crystals by recrystallization from ethanol and characterized by ^{1}H NMR spectroscopy and elemental analyses.



Scheme 2 *L1*, *C1*, Y=H; *L2*, *C2*, Y=Cl; *L3*, *C3*, Y=OCH_3; *L4*, *C4*, Y=Br; *L5*, *C5*, Y=NO_2

The synthesis of *trans*-[Ru(bipy)L(Cl)$_2$] (*C1–C5*) was achieved by the stepwise equimolar addition of azoimine ligands, bipy and then an excess of lithium chloride (to prevent formation of the solvato complexes) as shown in Scheme 1. These neutral complexes are air stable both as solids and in solution. Their structures were confirmed by ^{1}H NMR spectra, elemental analysis and X-ray diffraction for complex *(C1).* As expected, magnetic susceptibility measurements show that these complexes are diamagnetic with low spin ruthenium(II). The aromatic region in the ^{1}H NMR spectra of complexes (*C1–C5*) consists of several coupled multiplets due to aromatic protons of the phenyl rings of the 2,2′-bipyridine and of the phenyl rings of the azoimine ligands. In their IR spectra, all the complexes show bands in the range of 1,660–1,712 cm^{-1} assignable to the C=O stretching frequency of the acetyl group. The intense bands in the ranges of 1,560–1,590 and 1,430–1,500 cm^{-1} are assigned to the C=N and N=N stretching bands of the azoimine ligands, respectively.

Crystal structures

Single crystals of (*C1*) were grown in dichloromethane/hexane solutions. The crystal data, including the data collection and structure refinement parameters, are presented in Table 1. Selected bond lengths and angles are summarized in Table 2. An ORTEP diagram of (*C1*) is given in Fig. 1. Complex (*C1*) crystallizes in the monoclinic space group *P*21/*n*. The X-ray crystal structure of (*C1*) shows that

Table 2 Selected bond lengths [Å] and angles [°] for (*C1*)

Bond lengths (Å)		Bond angles (°)			
Cl(1)–Ru(1)	2.3719(8)	N(18)–Ru(1)–N(25)	76.26(10)	N(1)–Ru(1)–Cl(2)	89.43(7)
Cl(2)–Ru(1)	2.3454(8)	N(18)–Ru(1)–N(12)	104.36(10)	N(18)–Ru(1)–Cl(1)	95.70(7)
N(1)–Ru(1)	2.127(2)	N(25)–Ru(1)–N(12)	178.63(9)	N(25)–Ru(1)–Cl(1)	95.26(7)
N(12)–Ru(1)	2.114(2)	N(18)–Ru(1)–N(1)	178.72(9)	N(12)–Ru(1)–Cl(1)	85.90(7)
N(18)–N(19)	1.313(3)	N(12)–Ru(1)–N(1)	76.34(9)	N(1)–Ru(1)–Cl(1)	85.41(7)
N(18)–Ru(1)	1.948(2)	N(18)–Ru(1)–Cl(2)	89.53(7)	Cl(2)–Ru(1)–Cl(1)	172.68(3)
N(25)–Ru(1)	2.018(2)	N(25)–Ru(1)–Cl(2)	90.95(7)	N(25)–Ru(1)–N(1)	103.01(9)
C(21)–N(25)	1.314(4)	N(12)–Ru(1)–Cl(2)	87.84(7)		

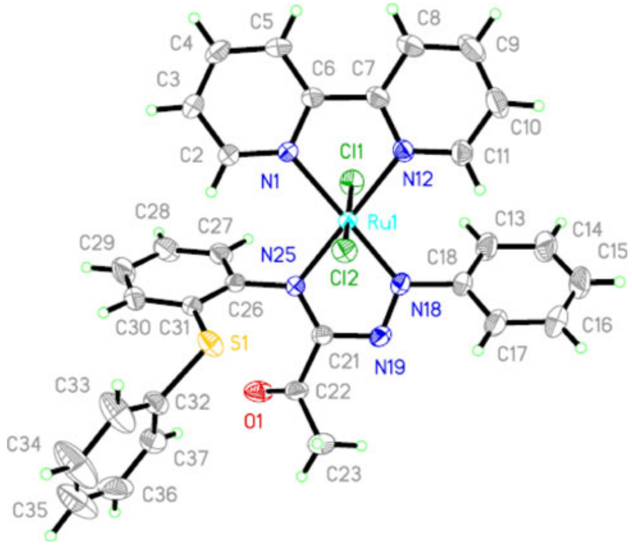


Fig. 1 Thermal ellipsoid plot (30%) of complex (*C1*)

Table 3 Cyclic voltammetry and electronic spectroscopy data of *trans*-[Ru(bipy)(L)(Cl)$_2$]

Complexes	Cyclic voltammetric data[a] ($E^{\mathrm{o}}_{1/2}$, *V*)[b]	Calculated E_{L}(L) for ligand L[c]	Electronic spectra λ_{max}(nm)[d]
C1	1.27	0.52	(510)
C2	1.30	0.56	(512)
C3	1.21	0.47	(516)
C4	1.27	0.52	(510)
C5	1.35	0.61	(510)

[a] Solvent acetonitrile, supporting electrolyte Bu$_4$NPF$_6$ (0.1 M), scan rate 0.1 V s, Pt-disk working electrode, Pt-wire auxiliary electrode, reference electrode Ag at 25 °C

[b] $E^{\mathrm{o}}_{1/2} = (E^{\mathrm{o}}_{\mathrm{pa}} + E^{\mathrm{o}}_{\mathrm{pc}})/2$

[c] Calculated using $E_{\mathrm{Ru(III/II)}} = 0.97[\sum E_{\mathrm{L}}] + 0.04$ in V vs. NHE, (E_{L} for bpy = 0.259 and for chloride = −0.24) [19]

[d] Solvent acetonitrile

the ruthenium atom is coordinated by four nitrogen and two chlorine atoms arranged in a distorted octahedron. The two Ru–N(L) distances (average 1.983 Å) are comparable to each other and are shorter than the average bond length for Ru–N(bipy) of 2.121 (2) Å. This shortening is assigned to strong back donation to the low-energy π^* orbital of the azoimine ligand (L). The two chlorine ligands are *trans* to each other with Ru–Cl(1) 2.3719(8) Å and Ru–Cl(2) 2.3454(8) Å bond distances, which are almost identical. These data are within the range of bond lengths found for similar Ru(II) complexes [16–18]. The angles around Ru vary from 172.68° for Cl-Ru–Cl to 178.67° for N–Ru–N. The chelate bite angles for N(18)–Ru(1)–N(25) and N(12)–Ru(1)–N(1) are 76.26(10) and 76.34(9), respectively. X-ray diffraction analyses show that there are no direct metal–S interactions in these complexes.

Electrochemistry and spectroscopy for the complexes

Cyclic voltammetric data (*C1–C5*) are presented in Table 3. Each complex shows a reversible response, due to Ru(III/II) couple in the potential range 1.27–1.35 V (Fig. 2). For each of the five complexes, the potential of the Ru(III/II) couple is sensitive to the nature of the substituents Y on the ligand. In the case of Y=NO$_2$, a higher oxidation potential value (1.35 V) of the Ru(III/II) couple is observed, whereas a lower Ru(III/II) oxidation potential (1.21 V) is observed for Y=OCH$_3$. Lever has developed an electrochemical parameterization method to calculate ruthenium(III/II) couples of complexes with octahedral geometry as shown in Eq. 1 [19];

$$E_{\mathrm{Ru(III/II)}} = 0.97\left[\sum E_{\mathrm{L}}\right] + 0.04 \tag{1}$$

where ΣE_{L} is the sum of electrochemical parameters (in V vs. NHE) for each ligand in the complex. The parameter E_L is a measure of the stabilizing effect a ligand has on the Ru(II) state, and so the greater the magnitude of positive E_{L}, the more positive the Ru(III/II) couples. Based on the previously found (E_{L}(bipy) = 0.259), E_{L}(Cl) = −0.24 [19]) and assuming ligand additivity, the Ru(III/II) couple for these octahedral complexes were used to calculate the

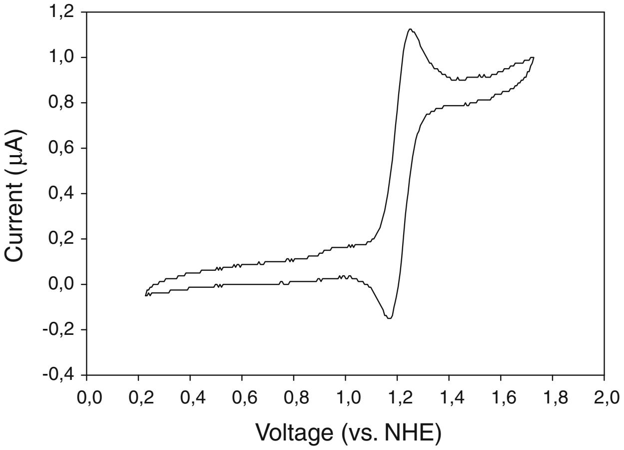


Fig. 2 Cyclic voltammogram for **C1** (solute concentration ~10^{-3} M) in acetonitrile 0.1 M TBAH at 25 °C, data reported in V vs. NHE with scan rate of 0.1 V/s

ligand (L) electrochemical parameters (E_L(L)), and the data are listed in Table 3.

Electronic spectral data for (*C1*–*C5*) (in acetonitrile) are collected in Table 3 and a representative spectrum of (*C1*) is shown in Fig. 3. All the complexes display four intense absorptions, two of which are in the visible region while the other two are extended to the UV region. The corresponding free ligands display two intense absorptions in the UV region, assigned to intraligand azoimine $\pi \rightarrow \pi^*$ transitions. These appear as a shoulder in the electronic spectra of the complexes, (*C1*–*C5*) with a minor shift in position, along with the absorption in the UV region. For the complexes, the visible region is dominated by a strong band centered at 509 nm ($\varepsilon = 6{,}870\ \mathrm{M^{-1}\ cm^{-1}}$) and a shoulder at 374 nm ($\varepsilon = 8710\ \mathrm{M^{-1}\ cm^{-1}}$), which we assign by analogy to other Ru(II) azoimine complexes to Ru(II)-to-azoimine $d\pi \rightarrow \pi^*$ MLCT transitions [20, 21].

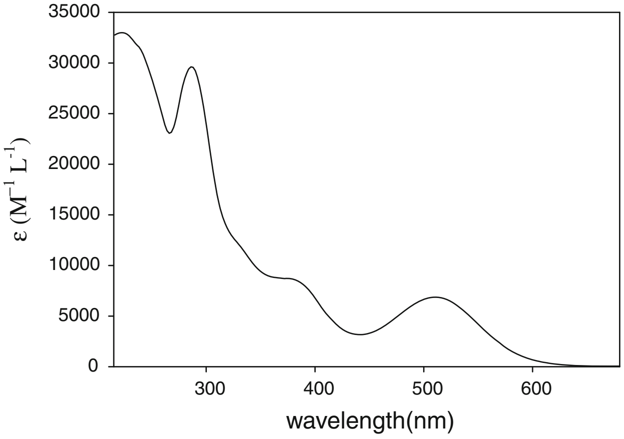


Fig. 3 Electronic spectra of **C1** in acetonitrile

Conclusions

Five ruthenium(II) complexes, of general formula *trans*-[Ru(bipy)L(Cl)$_2$], where L is a substituted phenylazo-(2-(phenylthio))phenylmethine ligand, were synthesized and characterized by spectroscopic, electrochemical and crystallographic methods. The crystal structure of *C1* reveals that there are no direct metal–S interactions. Cyclic voltammetric studies showed a reversible ruthenium-based oxidation process. The electronic effects of the substituents (Y) on the phenylazo-(2-(phenylthio))phenylmethine ligands are shown in the ruthenium couple, which is shifted to more positive potentials when stronger electron-withdrawing substituents are introduced. The electronic absorption spectra of these complexes showed two strong bands in the visible region, which were assigned to Ru(II)-to-azoimine $d\pi \rightarrow \pi^*$ MLCT transitions. The ligand electrochemical parameters for these new substituted phenylazo-(2-(phenylthio))phenylmethine ligands were calculated.

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