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Ruthenium Complexes with Chiral Tetradentate Imino–Sulfoxide Ligands

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Treatment of 2-(methylsulfinyl)benzaldehyde (**1**) with ethylenediamine or (1*R*,2*R*)-(–)-1,2-diaminocyclohexane afforded *N*,*N*′-bis[2-(methylsulfinyl)benzylidene]ethylenediamine (L^1) or (1*R*,2*R*)-*N*,*N*′-bis[2-(methylsulfinyl)benzylidene]-1,2-cyclohexanedia mine (L^2), respectively. Lithiation of 2-bromobenzaldehyde diethylacetal with *n*-BuLi/TMEDA followed by reaction with (*1R,2S,5R*)-(–)-menthyl-(*S*)-*p*-toluenesulfinate afforded 2-(*S*)-(*p*-tolylsulfinyl)benzaldehyde diethyl acetal (**2**). Deprotection of **2** with pyridinium tosylate followed by condensation with ethylenediamine, (1*R*,2*R*)-(–)-diaminocyclohexane, or (*S*,*S*)-(+)-diaminocyclohexane afforded *N*,*N*′-bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]ethylenediamine (L^3), (1*R*,2*R*)-*N*,*N*′-bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]-1,2-cyclohexanediamine ((*R*,*R*)-L^4), or (*S*,*S*)-*N*,*N*′-bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]-1,2-cyclohexanediamine ((*S*,*S*)-L^4), respectively. Treatment of $[Ru(PPh_3)_3Cl_2]$ with L afforded *trans*-$[Ru(L)Cl_2]$ [L = L^1 (**3**), L^2 (**4**), L^3 (**5**), (*R*,*R*)-L^4 ((*R*,*R*)-**6**), (*S*,*S*)-L^4 ((*S*,*S*)-**6**)]. The X-ray structures of (S_S,R_S)-**4**, (*R*,*R*)-**6**, and (*S*,*S*)-**6** have been determined. The average Ru–N, Ru–S, and Ru–Cl distances in (S_S,R_S)-**4** are 2.063, 2.2301, and 2.4039 Å, respectively. The corresponding distances in (*R*,*R*)-**6** are 2.071, 2.256, and 2.411 Å, and those in (*S*,*S*)-**6**, 2.058, 2.2275, and 2.3831 Å. Compound **3** exhibited a reversible Ru(III/II) couple at 0.56 V vs $Cp_2Fe^{+/0}$ in CH_2Cl_2. Treatment of **3** with $AgNO_3$ in water afforded the aqua compound *trans*-$[Ru(L^1)Cl(H_2O)][PF_6]$ (**7**), which has been characterized by X-ray crystallography. The Ru–Cl, Ru–O, average Ru–N, and average Ru–S distances in **7** are 2.3733(6), 2.1469(16), 2.071, and 2.2442 Å, respectively. Treatment of **3** with $AgNO_3$ followed by reaction with PPh_3 afforded $[Ru(L^1)(PPh_3)_2][PF_6]_2$ (**8**). Treatment of $[Os(PPh_3)_3Cl_2]$ with L^1 resulted in deoxygenation of one sulfoxide group of L^1 and formation of $[Os(L^5)Cl_2(PPh_3)]$ (**9**) (L^5 = *N*-[2-(methylsulfinyl)benzylidene]-*N*′-[2-(methylthio)benzylididene]ethylenediamine), which has been characterized by X-ray crystallography. The average Os–S(O), Os–N(trans to P), Os–N(trans to S), Os–P, and Os–Cl distances are 2.1931, 2.085, 2.175, 2.3641, and 2.4266 Å, respectively.

Introduction

Sulfoxides RR′S═O are ambidentate ligands that can bind to hard or soft metal ions via the oxygen or sulfur site, respectively, in accordance with the hard−soft acid base theory.[1] Redox- or photoinduced Ru−S to Ru−O linkage isomerization for sulfoxide ligands in Ru(II) pentaammine[2] and polypyridyl[3] complexes has been studied. However, recently it was found that Me_2SO also binds to Ru(III) and even Ru(IV) via the sulfur site, indicating that the sulfur σ-donation plays a role in the bonding in higher valent metal sulfoxide complexes.[4] While nonracemic sulfinyl groups have been widely used as chiral auxiliaries in stereoselective organic synthesis,[5] the use of optically pure sulfoxide ligands in asymmetric induction has not been well explored.[6−14] Metal-mediated enantioselective organic reactions, e.g. olefin

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hydrogenation,[6] addition of Et_2Zn to aldehydes,[8] allylic alkylation,[11−13] and transfer hydrogenation,[14] based on chiral bidentate sulfoxide ligands have been reported. Of special interest are Ru sulfoxide complexes that have been used as hydrogenation catalysts,[6] anticancer agents,[15] and precursors to metal-based radiosensitizers.[16] Ruthenium complexes containing optically active mondentate and bidentate sulfoxide ligands are well documented[6,17−19] and have been used as catalysts for asymmetric hydrogenation of olefins[6] and asymmetric epoxidation of olefins.[18] However, to our knowledge, ruthenium complexes with chiral tetradentate sulfoxide ligands have not been reported previously. We are particularly interested in ruthenium complexes with chelating sulfoxide-containing Schiff base ligands due to the reported catalytic activity of Ru(salen) complexes in a range of organic reactions including oxidation,[20,21] Diels−Alder reactions,[22,23] kinetic resolution of racemic epoxides,[23] cyclopropanation,[24] and trimethylsilylcyanation of aldehydes.[25] In this paper, we report on the synthesis of chiral tetradentate sulfoxide-containing Schiff base ligands. The preparations, crystal structures, and reactivity of ruthenium complexes with chiral tetradentate imino−sulfoxide ligands will be described.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 75.5, and 121.5 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C) and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, and mass spectra, on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

Materials. $[Ru(PPh_3)_3Cl_2]$,[26] $[Os(PPh_3)_3Cl_2]$,[27] (*R*,*R*)-1,2-diaminocyclohexane mono-L-(+)-tartrate, and (*S*,*S*)-1,2-diaminocyclohexane mono-D-(−)-tartrate[28] were synthesized according to literature methods. 2-(Methylthio)benzaldehyde and (1*R*,2*S*,5*R*)-(−)-menthyl-(*S*)-*p*-toluenesulfinate were obtained from Aldrich Ltd.

Synthesis of 2-(Methylsulfinyl)benzaldehyde (1). To a solution of 3-chloroperoxybenzoic acid (*m*-CPBA) (57%, 2.1 g, 6.94 mmol) in CH_2Cl_2 (5 mL) was added 2-(methylthio)benzaldehyde (0.9 mL, 6.98 mmol) at 0 °C. After the mixture was stirred at the same temperature for 3 h, it was quenched with saturated Na_2CO_3(aq) (15 mL) and extracted with CH_2Cl_2 (15 mL). The organic solution was washed with brine (2 × 15 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, eluant Et_2O/CH_2Cl_2 (1:1)) to afford a pale yellow solid (yield: 0.859 g, 73%). ^{1}H NMR ($CDCl_3$): δ 10.27 (s, 1 H), 8.41 (d, J = 7.2 Hz, 1H), 8.34 (dd, J = 7.5 and 7.2 Hz, 1H), 8.14 (td, J = 7.8 and 1.2 Hz, 1H), 7.98 (td, J = 7.5 and 1.2 Hz, 1H), 2.87 (s, 3H). MS (CI): *m*/*z* 168.9 ($M^+ + 1$).

Synthesis of *N*,*N*′-Bis[2-(methylsulfinyl)benzylidene]ethylenediamine (L^1). To **1** (0.51 g, 3.04 mmol) in MeOH (25 mL) was added 0.5 equiv of ethylenediamine (0.1 mL, 1.50 mmol), and the mixture was heated at reflux for 24 h. The solvent was pumped off, and the residue was purified by column chromatography (silica) using THF/Et_2O (2:1) as eluant to afford a pale yellow solid (yield: 0.463 g, 84%). ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1H), 8.64 (s, 1H), 8.55 (dd, J = 7.6, 2.4 Hz, 2H), 7.91−7.96 (m, 2H), 7.80−7.88 (m, 4H), 4.37−4.40 (m, 2H), 4.21−4.24 (m, 2H), 3.03 (s, 3H), 3.02 (s, 3H). MS (CI): *m*/*z* 361 ($M^+ + 1$).

Synthesis of (1*R*,2*R*)-*N*,*N*′-Bis[2-(methylsulfinyl)benzylidene]-1,2-cyclohexanediamine (L^2). A mixture of (*R*,*R*)-(−)-1,2-diaminocyclohexane mono-L-(+)-tartrate (0.207 g, 0.91 mmol) and Na_2CO_3 (0.19 g, 1.79 mmol) was added MeOH (10 mL) and H_2O (1 mL) at 0 °C, and the mixture was heated at reflux for 1.5 h. After the mixture was cooled to room temperature, **1** in MeOH (5 mL) was added at 0 °C and the new mixture was heated at reflux for 2 d. The resultant mixture was allowed to cool to room temperature, and the solvent was pumped off. The residue was dissolved in CH_2Cl_2, washed with brine (15 mL), dried over anhydrous $MgSO_4$, and purified by column chromatography (silica, eluant Et_2O/THF (1:1)) to afford a white solid (yield: 0.293 g, 78%). ^{1}H NMR ($CDCl_3$): δ 8.15−8.33 (m, 4H), 7.41−7.63 (m, 6H), 3.32−3.50 (m, 2H), 2.84, 2.81, 2.72, 2.70 (all singlets, 6H), 1.79−1.90 (m, 8 H). MS (CI): *m*/*z* 415 ($M^+ + 1$).

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Synthesis of 2-(*S*)-(*p*-Tolylsulfinyl)benzaldehyde Diethyl Acetal (2). To a solution of 2-bromobenzaldehyde diethyl acetal (0.4 mL, 2.02 mmol) in THF (10 mL) was added *n*-BuLi (1.30 mL of a 1 M solution in hexane, 2.08 mmol) at −78 °C. The mixture was stirred for 30 min, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.3 mL, 2.01 mmol) and (1*R*,2*S*,5*R*)-(−)-menthyl-(*S*)-*p*-toluenesulfinate (0.55 g, 1.87 mmol) were added at −78 °C. After being stirred for 3 h, the reaction was quenched by saturated NH_4Cl(aq) (10 mL). The aqueous layer was extracted into Et_2O (3 × 10 mL), washed with brine (3 × 20 mL), dried over anhydrous $MgSO_4$, and purified by column chromatography (silica, eluent Et_2O/hexane (1:1)) to afford a pale yellow oil (yield: 0.447 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.93 (d, J = 6.90 Hz, 1H), 7.63 (d, J = 7.20 Hz, 1H), 7.52 (d, J = 7.80 Hz, 2H), 7.47 (m, 2H), 7.19 (d, J = 7.80 Hz, 2H), 5.72 (s, 1H), 3.50−3.64 (m, 4H), 2.35 (s, 3H), 1.26 (t, J = 6.90 Hz, 3H), 1.09 (t, J = 6.90 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 143.8, 142.2, 140.9, 137.2, 130.7, 129.7, 129.6, 126.6, 125.6, 125.4, 98.8, 62.5, 61.8, 21.4, 15.2, 15.0. MS (CI): *m*/*z* 273 ($M^+ - OEt_2$).

Synthesis of *N*,*N*′-Bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]ethylenediamine (L^3). A mixture of **2** (0.168 g, 0.53 mmol) and pyridinium tosylate (0.1 g, 0.40 mmol) in water (1 mL) and acetone (15 mL) was heated at reflux for 16 h. Removal of the volatiles gave a pale yellow solid (ca. 0.1 g). To a stirred solution of this yellow solid (0.10 g, 0.41 mmol) in toluene (15 mL) was added 0.5 equiv of ethylenediamine (14 μL, 0.21 mmol), and the reaction mixture was heated at reflux for 4 h. Removal of the solvent gave a pale yellow solid, which was sufficiently pure for subsequent reactions (yield: 0.1 g, 95%). ^{1}H NMR ($CDCl_3$): δ 8.27 (d, J = 7.80 Hz, 2H), 8.20 (s, 2H), 7.61 (t, J = 7.20 Hz, 2H), 7.52 (d, J = 7.20 Hz, 2H), 7.48 (d, J = 7.20 Hz, 2H), 7.40 (d, J = 8.10 Hz, 4 H), 7.06 (d, J = 8.10 Hz, 4 H), 3.83 (s, 4H), 2.28 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 159.4, 145.2, 143.7, 140.6, 133.4, 131.0, 130.44, 130.38, 129.4, 128.9, 128.1, 126.0, 125.2, 60.9, 21.4. MS (CI): *m*/*z* 245 ($M^+ + 1$). $[\alpha]^{22}_D = -276°$ (c = 0.43, CH_2Cl_2).

Synthesis of (1*R*,2*R*)-*N*,*N*′-Bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]-1,2-cyclohexanediamine ((*R*,*R*)-L^4). A mixture of (*R*,*R*)-1,2-diaminocyclohexane mono-L-(+)-tartrate (60 mg, 0.21 mmol) and Na_2CO_3 (55 mg, 0.44 mmol) with added toluene (10 mL) and H_2O (1 mL) was heated at reflux for 1 h. After the mixture was cooled to room temperature, **2** (0.4 mmol) was added and the new mixture was heated at reflux for 22 h and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (10 mL), washed with brine (10 mL), dried over anhydrous $MgSO_4$, and purified by column chromatography (silica) to give a pale yellow solid (yield: 76.1 mg, 66%). ^{1}H NMR ($CDCl_3$): δ 8.40 (s, 2H), 8.15 (d, J = 7.50 Hz, 2H), 7.59 (d, J = 7.50 Hz, 2H), 7.53 (t, J = 7.50 Hz, 2H), 7.43 (d, J = 7.50 Hz, 2H), 7.38 (d, J = 8.10 Hz, 4 H), 6.97 (d, J = 8.10 Hz, 4 H), 3.34 (m, 2H), 2.23 (s, 6H), 1.17−1.93 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 157.8, 144.8, 143.6, 140.2, 133.7, 130.8, 130.7, 130.4, 129.2, 125.7, 125.1, 74.8, 32.4, 24.3, 21.3. MS (CI): *m*/*z* 567 ($M^+ + 1$). $[\alpha]^{22}_D = -384°$ (c = 0.25, CH_2Cl_2).

Synthesis of (1*S*,2*S*)-*N*,*N*′-Bis[2-(*S*)-(*p*-tolylsulfinyl)benzylidene]-1,2-cyclohexanediamine ((*S*,*S*)-L^4). This was prepared similarly as for (*R*,*R*)-L^4 using (*S*,*S*)-1,2-diaminocyclohexane mono-D-(−)-tartrate in place of (*R*,*R*)-1,2-diaminocyclohexane mono-L-(+)-tartrate. Yield: 50%. ^{1}H NMR ($CDCl_3$): δ 8.42 (s, 2H), 8.16 (d, J = 7.8 Hz, 2H), 7.51−7.62 (m, 4H), 7.38−7.46 (m, 6H), 6.98 (d, J = 8.1 Hz, 2H), 3.36 (m, 2H), 2.25 (s, 6H), 1.34−1.79 (m, 8H).

Synthesis of *trans*-[Ru(L)Cl_2] (L = L^{1-3}, (*R*,*R*)-L^4, (*S*,*S*)-L^4). To solution of L (0.57 mmol) in THF (20 mL) was added with 1.2 equiv of [Ru(PPh_3)$_3Cl_2$] (0.654 g, 0.68 mmol), and the reaction mixture was heated at reflux overnight. The orange precipitate was collected, washed with hexane/Et_2O (1:1), and dried under vacuum. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded orange or red crystals.

Characterization data for *trans*-[Ru(L^1)Cl_2] (**3**): orange crystals; yield 45%; ^{1}H NMR ($CDCl_3$) δ 8.86 (s, 2H), 8.57 (d, J = 7.9 Hz, 1H), 8.43 (d, J = 7.8 Hz, 1H), 7.90 (m, 3H), 7.60 (m, 4H), 4.14 (m, 4H,), 3.62 (s, 3H), 3.37 (s, 3H); MS (CI) *m*/*z* 532 (M^+); UV/vis (CH_2Cl_2) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 451 (2600). Anal. Calcd for $C_{18}H_{20}Cl_2N_2O_2RuS_2$·$CH_2Cl_2$: C, 37.0; H, 3.6; N, 4.5. Found: C, 38.1; H, 3.8; N, 4.7.

Characterization data for *trans*-[Ru(L^2)Cl_2] (**4**): orange crystals; yield 59%; ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 2H), 8.58 (d, J = 8 Hz, 2H), 7.94 (m, 2H), 3.97 (d, J = 8.4 Hz, 2H), 3.49 (s, 3H), 3.35 (s, 3H), 2.78 (d, J = 11.6 Hz, 2H), 2.13 (m, 2H), 1.87 (d, J = 9.6 Hz, 2H), 1.44 (m, 2H); MS (FAB) *m*/*z* 586 (M^+), 551 ($M^+ - Cl$); UV/vis (CH_2Cl_2) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 449 (2250). Anal. Calcd for $C_{22}H_{26}Cl_2N_2O_2RuS_2$: C, 45.1; H, 4.4; N, 4.8. Found: C, 43.5; H, 4.4; N, 4.8.

Characterization data for *trans*-[Ru(L^3)Cl_2] (**5**): red crystals; yield 60%; ^{1}H NMR ($CDCl_3$) δ 8.93 (s, 2H), 8.17 (d, J = 7.8 Hz, 2H), 7.61−7.70 (m, 8H), 7.40 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 4H), 4.51 (d, J = 7.4 Hz, 2H), 4.16 (d, J = 7.4 Hz, 2H). 2.27 (s, 6H); IR (KBr, cm^{-1}) 1071 ($\nu_{S=O}$); MS (FAB) *m*/*z* 683 (M^+). UV/vis (CH_2Cl_2) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 459 (3310). Anal. Calcd for $C_{30}H_{28}Cl_2N_2O_2RuS_2$: C, 52.6; H, 4.13; N, 4.0. Found: C, 52.0; H, 4.7; N, 3.6.

Characterization data for *trans*-[Ru{(*R*,*R*)-L^4}Cl_2] ((*R*,*R*)-**6**): red crystals; yield 75%; ^{1}H NMR ($CDCl_3$) δ 8.86 (s, 2H), 7.74 (d, J = 6.9 Hz, 3H), 7.65 (d, J = 7.8 Hz, 3H), 7.51 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.04 (d, J = 8.1 Hz, 4H), 6.77 (d, J = 7.5 Hz, 2H), 4.34 (m, 2H), 2.82 (m, 2H), 2.43 (s, 6H), 2.17 (m, 2H), 2.05 (m, 2H), 1.55 (m, 2H); MS (FAB) *m*/*z* 738 ($M^+ + 1$), 703 ($M^+ - Cl + 1$); UV/vis (CH_2Cl_2) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 466 (3620). Anal. Calcd for $C_{34}H_{34}Cl_2N_2O_2RuS_2$·$2CH_2Cl_2$: C, 47.6; H, 4.2; N, 3.1. Found: 49.2; H, 4.5; N. 2.9.

Characterization data for *trans*-[Ru{(*S*,*S*)-L^4}Cl_2] ((*S*,*S*)-**6**): red crystals; yield 55%; ^{1}H NMR ($CDCl_3$) δ 8.77 (s, 2H), 8.15 (d, J = 8.1 Hz, 2H), 7.65 (m, 6H), 7.40 (d, J = 8.4 Hz, 4H), 7.12 (d, J = 8.1 Hz, 4H), 4.05 (m, 2H), 2.78 (m, 2H), 2.62 (s, 6H), 1.40−2.15 (m, 6H); MS (FAB) *m*/*z* 737 (M^+), 703 ($M^+ - Cl + 1$); UV/vis (CH_2Cl_2) λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 455 (3610).

Synthesis of *trans*-[Ru(L^1)Cl(H_2O)][PF_6] (7). A mixture of **3** (0.15 g, 0.28 mmol) and $AgNO_3$ (0.14 g, 0.85 mmol) in H_2O (20 mL) was heated at reflux for overnight. The AgCl precipitate was filtered off, and excess NH_4PF_6 was added. The yellow solid was collected, washed with cold H_2O, and recrystallized from hot water in the presence of a few drops of HPF_6(aq) (yield: 0.14 g, 62%). ^{1}H NMR (acetone-d_6): δ 9.56 (s, 2H), 8.62 (d, J = 7.8 Hz, 2H), 8.08−8.26 (m, 6H), 4.61 (m, 4H), 3.83 (s, 6H). MS (FAB): *m*/*z* 515 ($M^+ - PF_6 + 1$). UV/vis (H_2O) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 357 (2490). Anal. Calcd for $C_{18}H_{22}ClF_6N_2O_3PRuS_2$·$H_2O$: C, 31.9; H, 3.6; N, 4.1. Found: C, 32.0; H, 3.3; N, 4.0.

Synthesis of [Ru(L^1)(PPh_3)$_2$][BF_4]$_2$ (8). To a solution of **3** (0.1 g, 0.17 mmol) in acetone (25 mL) was added with 3 equiv of $AgBF_4$ (0.099 g, 5.1 mmol). The reaction mixture was heated at reflux for 1 h and filtered. Excess PPh_3 (0.116 g, 0.44 mmol) was added to the filtrate, and the mixture was stirred at room temperature for overnight. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to afford an orange solid (yield: 0.11 g, 82%). ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 2H), 8.35 (d, J = 7.5 Hz, 2H), 7.10−8.00 (m, 52H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 11.04 (s, PPh_3). Anal. Calcd for $C_{58}H_{56}B_2F_8N_2P_2O_4RuS_2$: C, 57.4; H, 4.7; N, 2.3. Found: C, 58.2; H, 4.4; N, 2.0.

Table 1. Crystallographic Data and Experimental Details for *trans*-[Ru{(S_S,R_S)-L^2}Cl_2] ((S_S,R_S)-**4**), *trans*-[Ru{(*R*,*R*)-L^4}Cl_2]·$2CH_2Cl_2$ ((*R*,*R*)-**6**·$2CH_2Cl_2$), *trans*-[Ru{(*S*,*S*)-L^4}Cl_2]·C_6H_{14} ((*S*,*S*)-**6**·C_6H_{14}), *trans*-[Ru(L^1)(H_2O)Cl][PF_6]·H_2O (**7**·H_2O), and [Os(L^5)Cl_2(PPh_3)]·$1/2\times2.5CH_2Cl_2$ (**9**·$1/2\times2.5CH_2Cl_2$)

	(S_S,R_S)-**4**	(*R*,*R*)-**6**·$2CH_2Cl_2$	(*S*,*S*)-**6**·C_6H_{14}	**7**·H_2O	**9**·$1/2\times2.5CH_2Cl_2$
formula	$C_{22}H_{26}Cl_2N_2O_2RuS_2$	$C_{34}H_{34}Cl_2N_2O_2RuS_2$·$2CH_2Cl_2$	$C_{34}H_{34}Cl_2N_2O_2RuS_2$·$C_6H_{14}$	$C_{18}H_{22}ClF_6N_2O_3PRuS_2$·$H_2O$	$C_{72}H_{70}Cl_4N_4O_2Os_2P_2S_4$·$2.5CH_2Cl_2$
fw	756.39	908.57	824.89	678.00	1948.02
cryst system	monoclinic	triclinic	tetragonal	triclinic	Triclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P4_3$	$P\bar{1}$	$P\bar{1}$
a, Å	11.3306(7)	9.5800(19)	11.9009(4)	9.0506(5)	15.8687(10)
b, Å	10.7656(7)	10.250(2)	11.9009(4)	11.5196(7)	16.5049(10)
c, Å	12.2035(8)	11.570(2)	27.1190(13)	12.7984(8)	17.7119(11)
α, deg		68.34(3)		114.2560(10)	68.4310(10)
β, deg	102.5160(10)	71.42(3)		93.0420(10)	66.6190(10)
γ, deg		66.57(3)		99.7640(10)	67.4130(10)
V, Å^3	1453.22(16)	949.0(3)	3840.9(3)	1187.69(12)	3802.6(4)
Z	2	1	4	2	2
ρ_{calcd}, g cm^{-3}	1.729	1.590	1.427	1.896	1.701
temp, K	100(2)	160(2)	100(2)	100(2)	100(2)
μ(Mo Kα), mm^{-1}	1.262	0.981	0.693	1.093	3.855
F(000)	764	462	1712	680	1930
tot. reflcns	12482	5073	18640	7052	22490
indpdt reflcns	6553	4329	6272	5071	16372
R_{int}	0.0278	0.0496	0.0349	0.0150	0.0392
R1; wR2 ($I > 2\sigma(I)$)	0.0308, 0.0587	0.0516, 0.0988	0.0298, 0.0629	0.0282, 0.0682	0.0391, 0.0747
R1, wR2 (all data)	0.0388, 0.0614	0.0762, 0.1060	0.0354, 0.0643	0.0325, 0.0703	0.0629, 0.0781
GoF on F^2	1.023	0.964	1.093	1.056	0.998

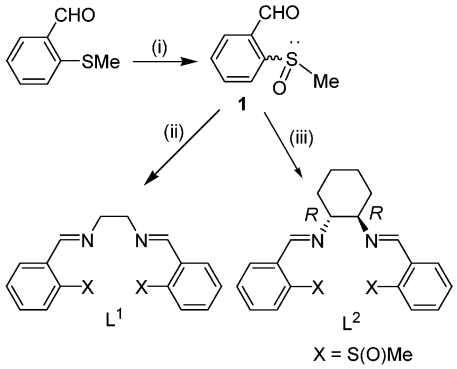
Synthesis of [Os(L^5)Cl_2(PPh_3)] (9) (L^5 = *N*-[2-(Methylsulfinyl)benzylidene]-*N*′-[2-(methylthio)benzylididene]ethylenediamine). A mixture of L^1 (0.08 g, 0.22 mmol) and [$OsCl_2$-(PPh_3)$_3$] (0.28 g, 0.26 mmol) in THF (20 mL) was heated at reflux for overnight. The solvent was pumped off under vacuum, and the residue was washed with hexane and recrystallized from CH_2Cl_2/hexane to give dark purple crystals which were suitable for X-ray diffraction study (yield: 0.09 g, 46%). ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 2H), 7.44−8.36 (m, 8H), 6.92−7.23 (m, 15H), 3.94−4.36 (m, 4H), 2.19 (s, 3H), 2.38 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −14.23 (s). MS (FAB): *m*/*z* 868 ($M^+ + 1$), 797 ($M^+ - 2Cl$), 606 ($M^+ - PPh_3$). Anal. Calcd for $C_{36}H_{35}ClN_2OOsPS_2$·CH_2Cl_2: C, 46.6; H, 3.9; N, 2.9. Found: C, 46.6; H, 4.0; N, 2.7.

X-ray Crystallography. A summary of crystallographic data and experimental details for complexes (S_S,R_S)-**4**, (*R*,*R*)-**6**·$2CH_2$-Cl_2, (*S*,*S*)-**6**·C_6H_{14}, **7**·H_2O, and **9**·$1/2\times2.5CH_2Cl_2$ are listed in Table 1. All intensity data were collected on a Bruker SMART-APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.701 73 Å). The data were integrated and sorted by using SAINT v6.26A software and were corrected for absorption by empirical methods. The structures were solved by direct methods and refined by full-matrix least-squares analyses on F^2. All non-hydrogen atoms were refined anisotropically with suitable restraints, except for those in the disordered hexane solvent molecule (C11S−C17S) in (*S*,*S*)-**6** and one disordered CH_2Cl_2 solvent molecule containing C3S in **9**·$1/2\times2.5CH_2Cl_2$, the site occupancy factor of which was fixed at 0.5. Calculations were performed using the SHELXTL[29] crystallographic software package. Selected bond lengths and angles for (S_S,R_S)-**4**, (*R*,*R*)-6·$2CH_2Cl_2$, (*S*,*S*)-**6**, **7**·H_2O, and **9**·$1/2\times2.5CH_2Cl_2$ are listed in Tables 2−6, respectively.

Results and Discussion

Ligand Syntheses. Oxidation of commercially available 2-(methylthio)benzaldehyde with *m*-CPBA at 0 °C afforded 2-(methylsulfinyl)benzaldehyde (**1**). Condensation of ethylenediamine with 2 equiv of **1** gave L^1 (Scheme 1).

Scheme 1 [a]



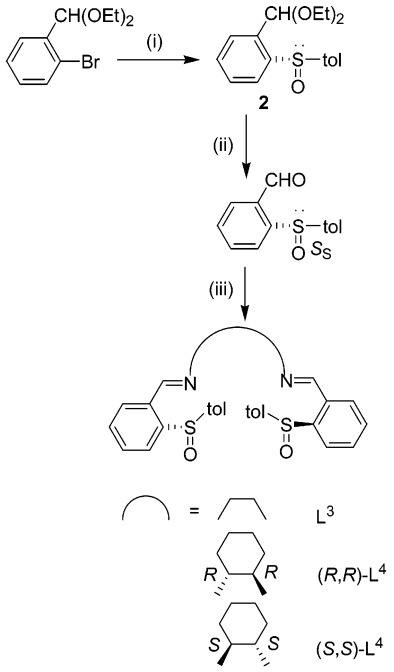
[a] Reagents and conditions: (i) *m*-CPBA, CH_2Cl_2, 0 °C; (ii) 0.5 equiv of ethylenediamine, toluene, reflux; (iii) 0.5 equiv of (1*R*,2*R*)-(−)-1,2-diaminocyclohexane mono-L-(+)-tartrate, Na_2CO_3, toluene/H_2O, reflux.

The ^{1}H NMR spectrum of L^1 in $CDCl_3$ showed two sets of resonant signals for the methyl (δ 3.02 and 3.03 ppm) and imine (N=C*H*) (δ 8.68 and 8.84 ppm) protons, presumably attributable to the meso (R_S,S_S) and racemic [(S_S,S_S) and (R_S,R_S)] isomers. Similarly, treatment of (1*R*,2*R*)-(−)-1,2-diaminocyclohexane with 2 equiv of **1** afforded L^2 (Scheme 1). In the ^{1}H NMR spectrum of L^2, the methyl protons appear as four singlets at δ 2.70, 2.72, 2.81 and 2.84 ppm, indicating that more than one diasteromer of L^2 was present in the sample. The imine protons appeared as an unresolved multiplet in δ 8.15−8.33 ppm. No attempts have been made to separate these diastereomers. However, it is clear that one of these diasteromers present should be (S_S,R_S)-L^2 according to the crystal structure of its Ru complex (vide infra).

To prepare Schiff base ligands containing optically active sulfoxide groups, nonracemic (*S*)-2-(*p*-tolysulfinyl)benzaldehyde was used as a precursor for the Schiff base synthesis. Lithiation of 2-bromobenzaldehyde diethyl acetal with *n*-BuLi/TMEDA, followed by reaction with (1*R*,2*S*,5*R*)-(−)-

(29) Sheldrick, G. M. *SHELXTL-97*; Universität Göttingen: Göttingen, Germany, 1997.

Scheme 2 [a]



[a] Reagents and conditions: (i) *n*-BuLi, TMEDA, (1*R*,2*S*,5*R*)-(−)-methyl-(*S*)-*p*-toluenesulfinate, THF, −78 °C; (ii) [pyH]OTs, acetone/H_2O, reflux; (iii) 0.5 equiv of diamine, toluene, reflux.

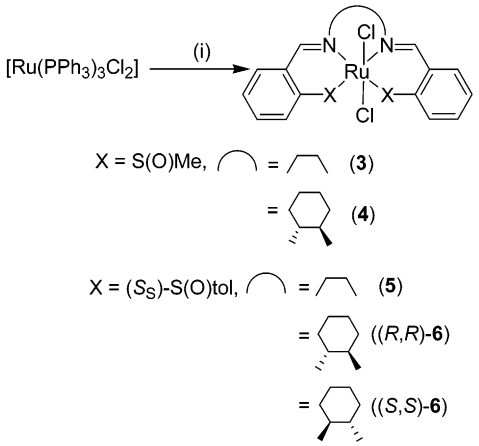
menthyl-(S)-*p*-toluenesulfinate afforded (*S*)-2-(*p*-tolylsulfinyl)-benzaldehyde diethyl acetal (**2**). Deprotection of **2** with pyridinium tosylate followed by condensation with ethylenediamine, (1*R*,2*R*)-(−)-1,2-diaminocycloehxane or (1*S*,2*S*)-(+)-1,2-diaminocyclohexane gave L^3, (*R*,*R*)-L,[4] or (*S*,*S*)-L,[4] respectively (Scheme 2).

As would be expected, only one set of NMR signals was observed for each of these ligands. The imine resonant signals for (*R*,*R*)-L^4 and (*S*,*S*)-L^4 were observed at δ 8.40 and 8.42 ppm, respectively. The configurations for both (*R*,*R*)-L^4 and (*S*,*S*)-L^4 have been unambiguously confirmed by X-ray diffraction studies on their ruthenium complexes (vide infra).

Ru(II) Dichloride Complexes. Ruthenium complexes containing tetradentate Schiff base ligands are of interest due to their reported catalytic activities toward organic reactions.[20−25] In this connection, ruthenium complexes with ligands L^1−L^4 were synthesized (Scheme 3).

Refluxing $[Ru(PPh_3)_3Cl_2]$ with L^1 or L^2 in THF gave air-stable *trans*-$[Ru(L^1)Cl_2]$ (**3**) or *trans*-$[Ru(L^2)Cl_2]$ (**4**), respectively. Complexes **3** and **4** are soluble in CH_2Cl_2 and polar solvents such as DMF, MeOH, and MeCN. Recrystallization of **4** from CH_2Cl_2/Et_2O/hexane afforded X-ray-quality single crystals. The ^1H NMR spectrum of recrystallized **3** in $CDCl_3$ shows a singlet at δ 8.86 pm due to the imine protons, suggesting that the sample contained predominately one diasteromer, possibly *trans*-$[Ru\{(R_S,S_S)\text{-}L^1\}Cl_2]$, according to the X-ray structure of its aqua derivative **7** (vide infra). The methyl protons in **3** appeared as two singlets with a relative intensity of 1:1 at δ 3.62 and 3.37 ppm, which are more downfield than those for uncomplexed L^1. A similar result was found for **4** (imine and methyl resonant signals at

Scheme 3 [a]



[a] Reagents and conditions: (i) L = L^1, L^2, L^3, (*R*,*R*)-L^4, or (*S*,*S*)-L^4; THF, reflux.

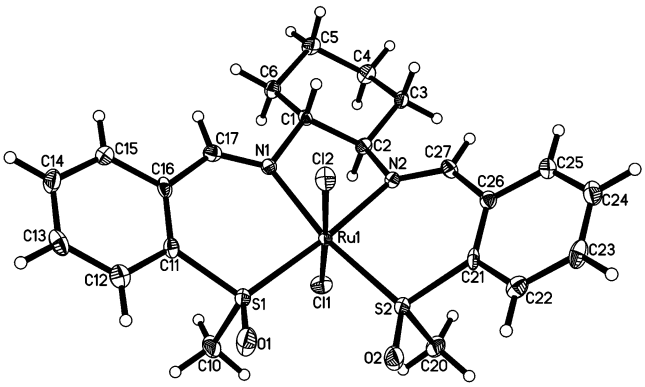


Figure 1. Molecular structure of *trans*-$[Ru\{(S_S,R_S)\text{-}L^2\}Cl_2]$ ((S_S,R_S)-**4**). Thermal ellipsoids are drawn at the 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$[Ru\{(S_S,R_S)\text{-}L^2\}Cl_2]$ ((S_S,R_S)-**4**)

Ru(1)−N(1)	2.058(3)	Ru(1)−N(2)	2.068(3)
Ru(1)−S(2)	2.2231(9)	Ru(1)−S(1)	2.2371(9)
Ru(1)−Cl(1)	2.4021(9)	Ru(1)−Cl(2)	2.4057(8)
S(1)−O(1)	1.468(3)	S(2)−O(2)	1.469(3)
N(1)−Ru(1)−N(2)	81.94(11)	N(1)−Ru(1)−S(2)	171.37(8)
N(2)−Ru(1)−S(2)	89.66(8)	N(1)−Ru(1)−S(1)	94.70(8)
N(2)−Ru(1)−S(1)	176.43(8)	S(2)−Ru(1)−S(1)	93.74(3)
N(1)−Ru(1)−Cl(1)	88.99(8)	N(2)−Ru(1)−Cl(1)	86.66(8)
S(2)−Ru(1)−Cl(1)	92.51(3)	S(1)−Ru(1)−Cl(1)	92.12(3)
N(1)−Ru(1)−Cl(2)	85.34(8)	N(2)−Ru(1)−Cl(2)	89.49(8)
S(2)−Ru(1)−Cl(2)	92.65(3)	S(1)−Ru(1)−Cl(2)	91.41(3)
Cl(1)−Ru(1)−Cl(2)	173.54(3)		

δ 8.75 and 3.49 and 3.35 ppm, respectively). The solid-state structure of **4** has been established by X-ray crystallography. As would be expected the sulfoxide groups in **4** are S-bonded. The crystal of **4** that was subjected to X-ray diffraction study was found to exhibit a meso (S_S,R_S) configuration. Figure 1 shows a perspective view of (S_S,R_S)-**4**·CH_2Cl_2; selected bond lengths and angles are listed in Table 2. The geometry around Ru is pseudo octahedral with the two mutually trans chloride ligands. The Ru−N distances (2.068(3) and 2.058(3) Å) in (S_S,R_S)-**4** are similar to those in *trans*-[Ru(Busalen)(NO)Cl] (Busalen = (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine, 2.00-(1) and 2.00(2) Å, respectively).[30] The Ru−S (2.2231(9) and

2.2371(9) Å) and Ru−Cl (2.4021(9) and 2.4057(8) Å) are comparable to those in *trans*-[Ru(Me_2SO)$_4$Cl$_2$] (2.2352(2) and 2.402(2) Å, respectively).[31] The average S−O distance of 1.4685 Å is shorter than that for free Me_2SO (1.492(2) Å).[1b] Consistent with the X-ray structural data, the IR $\nu_{S=O}$ for (S_S,R_S)-**4** was observed at 1098 cm^{-1}, which is ca. 76 cm^{-1} higher than that for uncomplexed L^2. The increase in S=O bond strength upon metal complexation for L^2 is typical for S-bonded sulfoxide ligands.[1] The UV−visible spectrum of **3** in CH_2Cl_2 shows an absorption at 451 nm (ϵ = 2600 M^{-1} cm^{-1}), which is tentatively assigned as a charge-transfer transition. A similar charge-transfer band has been observed for a Ru(II) complex with a related tetradentate thioether-containing Schiff base ligand [Ru(btb-en)Cl$_2$] (btb-en = *N*,*N*′-bis(2-*tert*-butylthiobenzylidene)-1,2-ethanediamine, λ_{max} = 503 nm).[32] The cyclic voltammogram of **3** shows a reversible couple at ca. 0.56 V vs $Cp_2Fe^{+/0}$, which is assigned as the metal-centered Ru(III/II) couple because uncomplexed L^1 is redox-inactive under the experimental conditions (−1.8 to +1.0 V vs $Cp_2Fe^{+/0}$). The Ru(III/II) couple for **4** was observed at a similar potential (0.6 V). The Ru(III/II) potential for complex **3** is considerably higher than that for the related thioether complex [Ru(btb-en)Cl$_2$] (0.14 V),[32] indicative of the π-acidity of the sulfoxide group. The relatively high Ru(III/II) potentials of **3** and **4** account for the air stability of the complexes.

Similarly, treatment of [Ru(PPh$_3$)$_3$Cl$_2$] with chiral L^3, (*R*,*R*)-L^4, or (*S*,*S*)-L^4 in THF afforded air-stable *trans*-[Ru(L^3)Cl$_2$] (**5**), *trans*-[Ru{(*R*,*R*)-L^4}Cl$_2$] ((*R*,*R*)-**6**), or *trans*-[Ru{(*S*,*S*)-L^4}Cl$_2$] ((*S*,*S*)-**6**), respectively. The imine proton resonant signals for complexes **5**, (*R*,*R*)-**6**, and (*S*,*S*)-**6** were found at δ 8.93, 8.86, and 8.77 ppm, respectively, which are more downfield than those for the corresponding uncomplexed ligands. The absorption maxima for **5**, (*R*,*R*)-**6**, and (*S*,*S*)-**6** at 459, 466 and 455 nm, respectively, are slightly red-shifted relative to those for **3** and **4**. Recrystallization of (*R*,*R*)-**6** and (*S*,*S*)-**6** from CH_2Cl_2/Et_2O/hexane afforded X-ray-quality red single crystals. The configuration and the binding mode of the sulfoxide ligands in (*R*,*R*)-**6** and (*S*,*S*)-**6** have been unambiguously established by X-ray crystallography. Molecular structures of (*R*,*R*)-**6** and (*S*,*S*)-**6** are shown in Figures 2 and 3, respectively. The corresponding selected bond lengths and angles are listed in Tables 3 and 4. For both complexes, the geometry around Ru is approximately octahedral with two mutually trans chloride ligands. The structures of the two complexes are very similar apart from the cyclohexylene ring of the ligand, which is the mirror image of each other. The average Ru−N, Ru−S, and Ru−Cl distances in (*R*,*R*)-**6** of 2.071, 2.256, and 2.411 Å, respectively, are similar those in (S_S,R_S)-**4**. The corresponding bond distances in (*S*,*S*)-**6** are 2.058, 2.2275, and 2.3831 Å. The S=O distances in (*R*,*R*)- and (*S*,*S*)-**6** are shorter than those for free Me_2SO, typical for S-bonded sulfoxide ligands.[1]

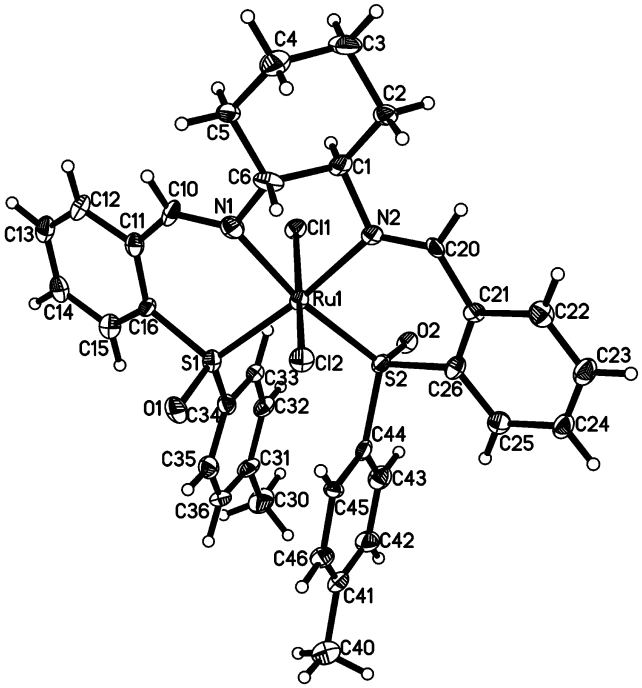


Figure 2. Molecular Structure of *trans*-[Ru{(*R*,*R*)-L^4}Cl$_2$] ((*R*,*R*)-**6**). Thermal ellipsoids are drawn at the 50% probability.

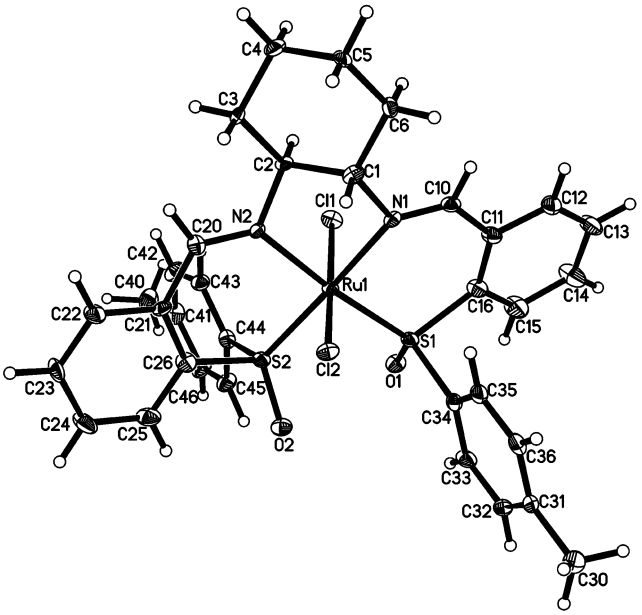


Figure 3. Molecular Structure of *trans*-[Ru{(*S*,*S*)-L^4}Cl$_2$] ((*S*,*S*)-**6**). Thermal ellipsoids are drawn at the 50% probability.

Ru(II) Aquo Complex. Heating **3** with $AgNO_3$ in water followed by precipitation with NH_4PF_6 afforded *trans*-[Ru(L^1)Cl(H$_2$O)][PF$_6$] (**7**). Complex **7** is soluble in both water and polar organic solvents such as acetone and DMF. Similarly, water-soluble *trans*-[Ru(L^2)(H$_2$O)Cl]$^+$ was prepared from **4** and $AgNO_3$ in water. Treatment of **5** or (*R*,*R*)-**6** with Ag(OTf) in CH_2Cl_2 gave insoluble yellow materials, which have yet to be characterized. The optical spectrum of **7** in water shows an absorption peak at ca. 357 nm that is at a higher energy than that for **3**. Attempts to remove the

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(31) Alessio, E.; Mestroni, G.; Nardin, G.; Attia, W. M.; Calligaris, M.; Sava, G.; Zorzet, S. *Inorg. Chem.* **1988**, *27*, 4099.
(32) Nakajima, K.; Ando, Y.; Mano, H.; Kojima, M. *Inorg. Chim. Acta* **1998**, *274*, 184.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Ru{(*R*,*R*)-L^4}Cl$_2$] ((*R*,*R*)-**6**)

Ru(1)−N(1)	2.070(9)	Ru(1)−N(2)	2.072(9)
Ru(1)−S(1)	2.250(3)	Ru(1)−S(2)	2.261(3)
Ru(1)−Cl(1)	2.404(3)	Ru(1)−Cl(2)	2.418(3)
S(1)−O(1)	1.479(6)	S(2)−O(2)	1.485(6)
N(1)−Ru(1)−N(2)	81.6(3)	N(1)−Ru(1)−S(1)	90.3(2)
N(2)−Ru(1)−S(1)	171.4(2)	N(1)−Ru(1)−S(2)	171.2(3)
N(2)−Ru(1)−S(2)	90.5(2)	S(1)−Ru(1)−S(2)	97.79(10)
N(1)−Ru(1)−Cl(1)	82.7(2)	N(2)−Ru(1)−Cl(1)	88.8(2)
S(1)−Ru(1)−Cl(1)	93.00(9)	S(2)−Ru(1)−Cl(1)	93.24(9)
N(1)−Ru(1)−Cl(2)	89.1(2)	N(2)−Ru(1)−Cl(2)	84.3(2)
S(1)−Ru(1)−Cl(2)	92.83(10)	S(2)−Ru(1)−Cl(2)	94.08(10)
Cl(1)−Ru(1)−Cl(2)	169.94(10)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Ru{(*S*,*S*)-L^4}Cl$_2$] ((*S*,*S*)-**6**)

Ru(1)−N(1)	2.056(3)	Ru(1)−N(2)	2.060(3)
Ru(1)−S(1)	2.2258(9)	Ru(1)−S(2)	2.2292(9)
Ru(1)−Cl(1)	2.3799(8)	Ru(1)−Cl(2)	2.3862(9)
S(1)−O(1)	1.467(2)	S(2)−O(2)	1.478(3)
N(1)−Ru(1)−N(2)	82.13(11)	N(1)−Ru(1)−S(1)	93.91(8)
N(2)−Ru(1)−S(1)	175.02(8)	N(1)−Ru(1)−S(2)	174.45(8)
N(2)−Ru(1)−S(2)	94.10(8)	S(1)−Ru(1)−S(2)	90.07(3)
N(1)−Ru(1)−Cl(2)	89.51(8)	N(2)−Ru(1)−Cl(2)	84.72(8)
S(1)−Ru(1)−Cl(2)	98.31(3)	S(2)−Ru(1)−Cl(2)	86.08(3)
N(1)−Ru(1)−Cl(1)	85.01(8)	N(2)−Ru(1)−Cl(1)	89.52(8)
S(1)−Ru(1)−Cl(1)	87.12(3)	S(2)−Ru(1)−Cl(1)	99.07(3)
Cl(2)−Ru(1)−Cl(1)	172.55(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Ru(L^1)(Cl)(H$_2$O)][PF$_6$] (**7**)

Ru(1)−N(1)	2.065(2)	Ru(1)−N(2)	2.076(2)
Ru(1)−O(1)	2.1469(16)	Ru(1)−S(2)	2.2428(6)
Ru(1)−S(1)	2.2456(6)	Ru(1)−Cl(1)	2.3733(6)
S(1)−O(2)	1.4927(18)	S(2)−O(3)	1.4957(18)
N(1)−Ru(1)−N(2)	81.79(8)	N(1)−Ru(1)−O(1)	88.09(7)
N(2)−Ru(1)−O(1)	88.17(7)	N(1)−Ru(1)−S(2)	172.10(6)
N(2)−Ru(1)−S(2)	90.32(6)	O(1)−Ru(1)−S(2)	92.19(5)
N(1)−Ru(1)−S(1)	89.50(6)	N(2)−Ru(1)−S(1)	171.29(6)
O(1)−Ru(1)−S(1)	91.39(5)	S(2)−Ru(1)−S(1)	98.38(2)
N(1)−Ru(1)−Cl(1)	87.71(5)	N(2)−Ru(1)−Cl(1)	88.81(5)
O(1)−Ru(1)−Cl(1)	175.14(5)	S(2)−Ru(1)−Cl(1)	91.64(2)
S(1)−Ru(1)−Cl(1)	91.02(2)		

second chloride ligand in **7** using excess $AgNO_3$ or longer reaction time were unsuccessful. Recrystallization of **7** from water afforded single crystals of **7**·H$_2$O that has been characterized by X-ray diffraction. Figure 4 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 5. In the solid-state structure of **7**·H$_2$O, hydrogen bonds were found between cocrystallized water molecules and the cations [Ru(L^1)Cl(H$_2$O)]$^+$ (via the S═O groups and the aqua ligands), as well as among the cations [Ru(L^1)Cl(H$_2$O)]$^+$.[33] The geometry around Ru in **7** is pseudooctahedral with the aquo ligand trans to the chloride. Like (*S*$_S$,*R*$_S$)-**4**, for the crystal of **7** subjected to X-ray diffraction, the ligand L^1 in [Ru(L^1)(H$_2$O)Cl]$^+$ shows a meso configuration for the sulfoxide groups. The average Ru−N and Ru−S distances (2.071 and 2.2442 Å) are similar to those in (*S*$_S$,*R*$_S$)-**4**. The Ru−O(aqua) distance (2.1469(16) Å) is normal by comparison with other Ru(II) aqua compounds (e.g. 2.122(16) Å in [Ru(H$_2$O)$_6$]$^{2+}$[34]). The Ru−Cl

(33) A crystal packing diagram and hydrogen bond distances and angles for **7**·H$_2$O are given in Supporting Information.

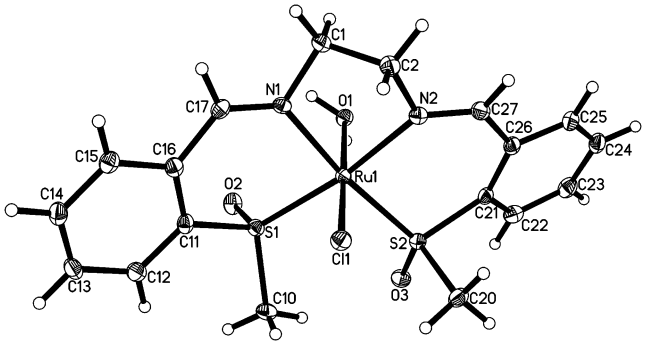
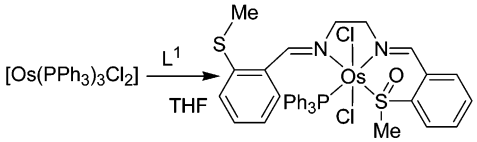


Figure 4. Molecular Structure of *trans*-[Ru(L^1)Cl(H$_2$O)][PF$_6$] (**7**). Thermal ellipsoids are drawn at the 50% probability.

Scheme 4



[Os(L^5)Cl$_2$(PPh$_3$)] (**9**)

distance (2.3733(6) Å) is slightly shorter than that in **1** due to the cationic nature of the complex and/or weaker trans influence of the aquo ligand compared with that of chloride.

Treatment of **7** with pyridine in H_2O led to an immediate color change from orange to yellow. However, no pyridine was found in the product after workup; only the starting material was recovered. Therefore, it seems likely that the pyridine deprotonated instead of displacing the aquo ligand in **7**. Indeed, a similar result was found when **7** was treated with NaOH(aq). The chloride ligand in **7** could, however, be replaced by tertiary phosphines such as PPh_3. Thus, treatment of **3** with excess $AgNO_3$ followed by addition of PPh_3 afforded the bis(phosphine) complex [Ru(L^1)(PPh$_3$)$_2$]-[PF$_6$]$_2$ (**8**).

Osmium(II) Complex. Treatment of [Os(PPh$_3$)$_3$Cl$_2$] with L^1 resulted in deoxygenation of one sulfoxide group in L^1 and the formation of red [Os(L^5)Cl$_2$(PPh$_3$)] (**9**), which contains a tridentate *N*,*N*,*S*(*O*) ligand L^5 (Scheme 4).

Complex **9** is air stable in both the solid state and solutions. It seems likely that the reduction of the sulfoxide group in L^1, possibly by dissociated PPh_3, was mediated by Os(II). Metal-mediated oxo transfer reactions between sulfoxides and phosphines are well documented.[35] No deoxygenation of L^1 had occurred for the reaction with Ru(II) obviously because of the lower reducing power Ru(II) compared with that of Os(II). Recrystallization of **9** from CH_2Cl_2/Et_2O afforded single crystals that were suitable for X-ray diffraction. The asymmetric unit of **9** was found to contain two independent molecules. Figure 5 shows the structure of one of the two independent molecules; selected bond lengths and angles are listed in Table 6. The geometry around Os is pseudooctahedral with two mutually trans chloride ligands. The Os−N(trans to sulfoxide) (average 2.175 Å) is longer than that Os−N(trans to PPh_3) (average 2.085 Å), indicating

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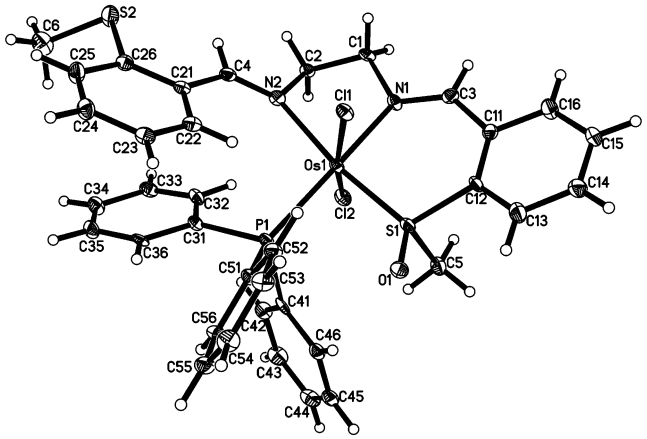

Figure 5. Molecular Structure of $[Os(L^5)Cl_2(PPh_3)]$ (**9**). Thermal ellipsoids are drawn at the 50% probability.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$[Os(L^5)Cl_2(PPh_3)]$ (**9**)

Os(1)−N(1)	2.069(4)	Os(2)−N(1A)	2.100(5)
Os(1)−N(2)	2.168(5)	Os(2)−N(2A)	2.181(4)
Os(1)−S(1)	2.1880(16)	Os(2)−S(1A)	2.1982(14)
Os(1)−P(1)	2.3506(15)	Os(2)−P(2)	2.3776(16)
Os(1)−Cl(1)	2.4172(13)	Os(2)−Cl(4)	2.4300(14)
Os(1)−Cl(2)	2.4271(14)	Os(2)−Cl(3)	2.4319(14)
S(1)−O(1)	1.477(4)	S(1A)−O(1A)	1.472(4)
N(1)−Os(1)−N(2)	79.66(18)	N(1A)−Os(2)−N(2A)	78.95(18)
N(1)−Os(1)−S(1)	92.91(14)	N(1A)−Os(2)−S(1A)	93.14(13)
N(2)−Os(1)−S(1)	171.21(13)	N(2A)−Os(2)−S(1A)	172.01(14)
N(1)−Os(1)−P(1)	172.28(12)	N(1A)−Os(2)−P(2)	175.57(13)
N(2)−Os(1)−P(1)	97.84(12)	N(2A)−Os(2)−P(2)	99.20(13)
S(1)−Os(1)−P(1)	90.13(5)	S(1A)−Os(2)−P(2)	88.78(5)
N(1)−Os(1)−Cl(1)	81.99(12)	N(1A)−Os(2)−Cl(4)	88.01(12)
N(2)−Os(1)−Cl(1)	86.69(12)	N(2A)−Os(2)−Cl(4)	87.21(12)
S(1)−Os(1)−Cl(1)	87.64(5)	S(1A)−Os(2)−Cl(4)	93.66(5)
P(1)−Os(1)−Cl(1)	105.23(5)	P(2)−Os(2)−Cl(4)	87.88(5)
N(1)−Os(1)−Cl(2)	85.28(12)	N(1A)−Os(2)−Cl(3)	79.94(12)
N(2)−Os(1)−Cl(2)	90.32(12)	N(2A)−Os(2)−Cl(3)	90.47(12)
S(1)−Os(1)−Cl(2)	93.76(5)	S(1A)−Os(2)−Cl(3)	87.03(5)
P(1)−Os(1)−Cl(2)	87.44(5)	P(2)−Os(2)−Cl(3)	104.17(5)
Cl(1)−Os(1)−Cl(2)	167.25(5)	Cl(4)−Os(2)−Cl(3)	167.95(5)

that the sulfoxide group has a stronger trans influence than PPh_3 with respect to Os(II). The average Os−S distance of 2.1931 Å is shorter than that in *trans*-$[Os(Me_2SO)_4Br_2]$ (2.351(2) Å), in which the trans Me_2SO ligands compete for back-bonding with each other.[36] The average Os−Cl and Os−P distances (average 2.4266 and 2.3641 Å, respectively) in **9** are normal by comparison with other Os(II) phosphine complexes (e.g. 2.434 and 2.348−2.372 Å, respectively, in *trans*-$[Os(dppe)Cl_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$)).[37] The average S−O distance in **9** (1.475 Å) is shorter than that in free Me_2SO (1.492(2) Å), characteristic for S-bonded sulfoxide ligand.[1b]

Conclusions. We have synthesized and characterized the first ruthenium complexes with chiral tetradentate sulfoxide-containing Schiff base ligands. The configuration and S-bonding mode of the tetradentate sulfoxide ligands in these complexes have been unambiguously established by X-ray diffraction studies. Cyclic voltammetry indicated that the sulfoxide groups in these ligands are strong π acceptors that can stabilize the Ru(II) state. On the other hand, reaction of the tetradentate sulfoxide ligand with Os(II) resulted in deoxygenation of the sulfoxide group and formation of an Os(II) complex with a tridentate *N*,*N*,*S*(*O*) ligand. A water-soluble Ru(II) aqua complex containing a tetradentate sulfoxide ligand has been synthesized and structurally characterized. The study of catalytic activity of the newly prepared Ru and Os sulfoxide complexes is underway.

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Supporting Information Available: Listings of final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles of (*S*$_S$,*R*$_S$)-**4**, (*R*,*R*)-**6**·$2CH_2Cl_2$, (*S*,*S*)-**6**·C_6H_{14}, **7**·H_2O, and **9**·$1/2\times2.5CH_2Cl_2$, a crystal packing diagram for **7**·H_2O, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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