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Research paper

Synthesis, characterization and crystal structures of ruthenium complexes with bidentate chiral salicylaldiminato ligands

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ABSTRACT

Condensations of salicylaldehyde and 4-chlorosalicylaldehyde with (*R*)-α-methylbenzylamine in refluxing ethanol afforded the chiral Schiff base ligands (*R*)-*N*-(1-phenylethyl)salicylidene (**HL1**∗) and (*R*)-*N*-(1-phenylethyl)(4-chlorosalicylidene) (**HL2**∗), respectively. Similarly, reaction of 3,5-di-*tert*-butylsalicylaldehyde and (*S*)-2-amino-3-methylbutan-1-ol gave the chiral Schiff base ligand (*S*)-*N*-(1-hydroxymethylisobutyl)(3,5-di-*tert*-butylsalicylidene) (**HL3**∗). Treatment of $(Et_4N)[RuCl_4(MeCN)_2]$ and $[RuCl_3(NO)(PPh_3)_2]$ with **HL1**∗ in the presence of triethylamine afforded an anionic ruthenium(III) complex (*R*,*R*)-$(Et_4N)[Ru(\kappa^2\text{-}N,O\text{-}\mathbf{L1}*)_2Cl_2]$ (**1**) and a neutral ruthenium(II) nitrosyl complex (*R*)-$[Ru(\kappa^2\text{-}N,O\text{-}\mathbf{L1}*)(NO)Cl_2(PPh_3)]$ (**2**), respectively. Interaction of $[RuCl_2(PPh_3)_3]$ and 2 equiv. **HL2**∗ led to isolation of a ruthenium(III) complex (*R*,*R*)-$[Ru(\kappa^2\text{-}N,O\text{-}\mathbf{L2}*)_2Cl(PPh_3)]$ (**3**). Reaction of $[Ru(NO)Cl_3{\cdot}xH_2O]$ and **HL3**∗ gave an anionic ruthenium(II) nitrosyl complex (*S*)-$(Et_3NH)[Ru(\kappa^2\text{-}N,O\text{-}\mathbf{L3}*)(NO)Cl_3]$ (**4**). The molecular structures of ligands **HL1**∗, **HL2**∗ and ruthenium complexes **1**–**4** have been determined by single-crystal X-ray crystallography.

1. Introduction

The catalytic potential of ruthenium complexes in organic syntheses has been well documented. As a result, chiral ruthenium complexes have attracted great attention in recent years and have been widely employed in many asymmetric organic transformation reactions [1,2]. On the other hand, the compounds (*R*)- and (*S*)-*N*-(1-phenylethyl)-salicylideneamine were recognized as versatile chiral ligands in coordination chemistry for its electric and steric properties could be easily adjusted by altering substituents on the aryl moiety. Many transition metal complexes, including Zn, Pd, Cu, V, Co, Ir, Rh, Os, Ti, Zr and Fe, have been reported to adopt the (*R*)- or (*S*)-*N*-(1-phenylethyl)-salicyli-deneamine ligands [3–11]. Typically, several diastereomeric and optically active arene-ruthenium(II) complexes of the type $[(\eta^6\text{-arene})Ru(LL*)L]$ and $[(\eta^6\text{-arene})Ru(LL*)L]X$ with (*S*)-*N*-(1-phenylethyl)salicylideneamine ligands were synthesized and structurally characterized during the last decades (arene = benzene and *p*-cymene, LL∗ = (*S*)-*N*-(1-phenylethyl)salicylideneamine, L = monodentate ligand or halide, X = anion) [12–18], whereas nitrosyl and triphenylphosphine ruthenium complexes with chiral (*R*)-*N*-(1-phenylethyl)salicylideneamine ligand was less investigated. Previously, we have reported a series of ruthenium(II)/ruthenium(III) complexes with bi-, tri- or tetra-dentate Schiff-base ligands [19–21], as our long-standing research interest in ruthenium complexes with the correspondingly catalytic properties, we disclose herein syntheses and structures of a series of cationic and neutral ruthenium(II)/(III) complexes with bidentate chiral Schiff base ligands derived from (*R*)-α-methylbenzylamine, (*S*)-2-amino-3-methylbutan-1-ol and substituted salicylaldehydes in this paper.

2. Experimental

2.1. General considerations

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. Triethylamine, salicylaldehyde, 4-chlorosalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde, (*R*)-α-methylbenzylamine, (*S*)-2-amino-3-methylbutan-1-ol were purchased from Alfa Aesar Ltd. and used without further purification. The chiral Schiff bases (**HL1**∗–**HL3**∗) were prepared by condensation of substituted salicylaldehydes and (*R*)-(+)-α-methylbenzylamine or (*S*)-2-amino-3-methylbutan-1-ol in the refluxing ethanol (Scheme 1) [6], of which single crystals of (*R*)-*N*-(1-phenylethyl)salicylideneamine (**HL1**∗) and (*R*)-*N*-(1-phenylethyl)(4-chlorosalicylideneamine) (**HL2**∗) were obtained from

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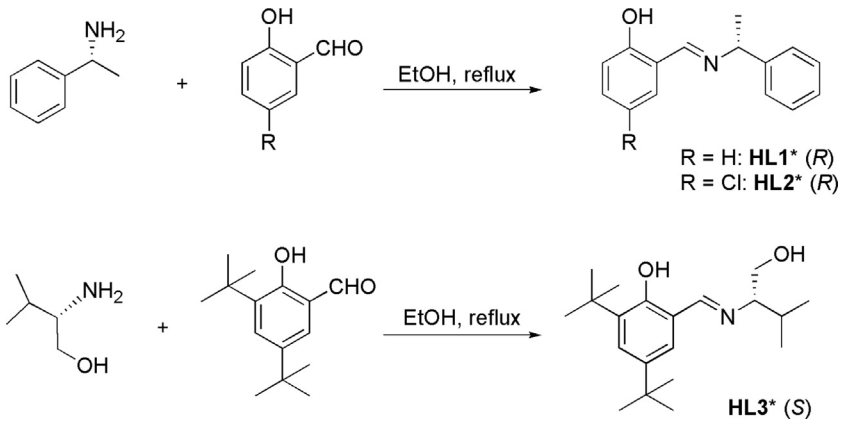

Scheme 1. Synthesis of chiral Schiff bases **HL1***, **HL2*** and **HL3***.

recrystallization of two chiral Schiff base ligands in methanol/diethyl ether (1:3). $(Et_4N)[RuCl_4(MeCN)_2]$ [22], $[RuCl_3(NO)(PPh_3)_2]$ [23], $[RuCl_2(PPh_3)_3]$ [24], and $[Ru(NO)Cl_3{\cdot}xH_2O]$ [25] were prepared according to the literature methods. NMR spectra were recorded on a Bruker ALX 400 Plus spectrometer operating at 400 MHz for ^1H and chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. The magnetic moment for the solid sample was measured by a Sherwood magnetic susceptibility balance at room temperature. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Synthesis of (R,R)-(Et$_4$N)[Ru(κ^2-N,O-**L1***)$_2$Cl$_2$] (**1**)

To a slurry of $(Et_4N)[RuCl_4(MeCN)_2]$ (113.8 mg, 0.25 mmol) in DMF (5 mL) was added a solution of **HL1*** (112 mg, 0.50 mmol) and Et_3N (56 mg, 0.50 mmol) in EtOH (5 mL), and then the mixture was heated at 90 °C with stirring overnight, during which there was a color change from light red to dark red. Addition of Et_2O (30 mL) to the reaction solution gave brown precipitate which was filtered and washed with Et_2O and hexane. The greenish brown precipitate was dissolved in CH_2Cl_2 (10 mL). The clearly brown filtrate was layered with Et_2O (20 mL) at room temperature, and greenish black block-shaped crystals of (Et$_4$N)[Ru(κ^2-N,O-**L1***)$_2$Cl$_2$] (**1**) were isolated in a week. Yield: 115 mg, 61% (based on Ru). μ_{eff} = 1.99 μ_B. IR (KBr disc, cm^{-1}): 3034, 2927, 2912 (ν_{C-H}), 1623 ($\nu_{C=N}$), 1236 (ν_{Ar-O}). MS (FAB): *m/z* 619 [Ru(κ^2-N,O-**L1***)$_2$Cl$_2$], 584 [Ru(κ^2-N,O-**L1***)$_2$Cl], 549 [Ru(κ^2-N,O-**L1***)$_2$]. *Anal.* Calc. for $C_{38}H_{48}N_3O_2Cl_2Ru$: C, 60.79; H, 6.44; N, 5.60%. Found: C, 60.71; H, 6.36; N, 5.64%.

2.3. Synthesis of (R)-[Ru(κ^2-N,O-**L1***)(NO)Cl$_2$(PPh$_3$)] (**2**)

A mixture of $RuCl_3(NO)(PPh_3)_2$ (190 mg, 0.25 mmol), **HL1*** (56 mg, 0.25 mmol) and Et_3N (28 mg, 0.25 mmol) in DMF (10 mL) was heated at 100 °C with stirring overnight, during which there was a color change from orange to red. Addition of Et_2O (30 mL) to the reaction solution gave red precipitate which was filtered and washed with Et_2O and hexane. The red precipitate was dissolved in CH_2Cl_2 (10 mL). The red filtrate was layered with Et_2O (10 mL) and hexane (20 mL) at room temperature, and red pillar-shaped crystals of [Ru(κ^2-N,O-**L1***)(NO)Cl$_2$(PPh$_3$)] (**2**) suitable for X-ray diffraction were obtained in five days. Yield: 126 mg, 73% (based on Ru). IR (KBr disc, cm^{-1}): 3031, 2924, 2908 (ν_{C-H}), 1867 ($\nu_{N=O}$), 1629 ($\nu_{C=N}$), 1236 (ν_{Ar-O}), 1437, 1075 and 691(ν_{PPh3}); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.26 (d, 3H, *J* = 6.8 Hz, CH_3), 5.56 (q, 1H, *J* = 6.0 Hz, C*H*), 6.63 (t, 2H, *J* = 5.4 Hz, Ar*H*), 6.75 (t, 2H, *J* = 5.6 Hz, Ar*H*), 6.94–7.33 (m, 5H, C*Ph*), 7.43–7.78 (m, 15H, P*Ph*$_3$), 8.29 (s, 1H, -C*H*=N) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 15.2 (s, PPh_3) ppm. MS (FAB): *m/z* 688 [M$^+$], 653 [M$^+$ − Cl], 618 [M$^+$ − 2Cl], 588 [M$^+$ − 2Cl − NO], 426 [M$^+$ − PPh_3], 326 [Ru(κ^2-N,O-**L1***)]$^+$. *Anal.* Calc. for $C_{33}H_{29}N_2O_2PCl_2Ru$: C, 57.56; H, 4.24; N, 4.07%. Found: C, 57.43; H, 4.22; N, 4.15%.

2.4. Synthesis of (R,R)-[Ru(κ^2-N,O-**L2***)$_2$Cl(PPh$_3$)] (**3**)

To a solution of $[RuCl_2(PPh_3)_3]$ (240 mg, 0.25 mmol) in THF (15 mL) was added a solution of **HL2*** (130 mg, 0.50 mmol) and Et_3N (56 mg, 0.50 mmol) in THF (5 mL), and then the mixture was stirred overnight at reflux, during which there was a color change from brown to dark green. After removal of solvent in *vacuo*, the residue was extracted with CH_2Cl_2 (5 mL × 2) and the solution was filtered. The filtrate was layered with Et_2O (20 mL) at room temperature, and dark green block-shaped crystals of [Ru(κ^2-N,O-**L2***)$_2$Cl(PPh$_3$)] (**3**) were obtained in three days. Yield: 108 mg, 47% (based on Ru). μ_{eff} = 1.97 μ_B. IR (KBr disc, cm^{-1}): 3024, 2921, 2904 (ν_{C-H}), 1621 ($\nu_{C=N}$), 1232 (ν_{Ar-O}), 1445, 1091 and 699 (ν_{PPh3}). MS (FAB): *m/z* 916 [M$^+$], 881 [M$^+$ − Cl], 654 [M$^+$ − PPh_3], 619 [Ru(κ^2-N,O-**L2***)$_2$]$^+$. *Anal.* Calc. for $C_{48}H_{41}N_2O_2PCl_3Ru$: C, 62.92; H, 4.51; N, 3.06%. Found: C, 62.67; H, 4.48; N, 3.02%.

2.5. Synthesis of (S)-(Et$_3$NH)[Ru(κ^2-N,O-**L3***)(NO)Cl$_3$] (**4**)

To a slurry of $Ru(NO)Cl_3{\cdot}xH_2O$ (68.4 mg, 0.25 mmol) in DMF (5 mL) was added a solution of **HL3*** (80 mg, 0.25 mmol) and a little excess of Et_3N (33.0 mg, 0.30 mmol) in THF (10 mL), and then the reaction mixture was heated at 90 °C with stirring for 4 h, during which time there was a color change from orange to red. Addition of Et_2O (40 mL) to the reaction solution gave red precipitate which was filtered and washed with Et_2O (5 mL × 2) and hexane (5 mL). The red precipitate was dissolved in CH_2Cl_2 (10 mL). The red filtrate was layered with THF (5 mL) and Et_2O (25 mL) at room temperature and red bar-shaped crystals of (Et$_3$NH)[Ru(κ^2-N,O-**L3***)$_2$(NO)Cl$_3$] (**4**) were isolated in three days. Yield: 120 mg, 73%. IR (KBr disc, cm^{-1}): 3441 (ν_{N-H}), 3278 (mbr, ν_{O-H}), 3031, 2934, 2912 (ν_{C-H}), 1869 ($\nu_{N=O}$), 1626 ($\nu_{C=N}$), 1239 (ν_{Ar-O}); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 9H, CH_3), 1.08 (s, 6H, CH(CH_3)$_2$), 1.32 (s, 18H, ^tBu), 1.95 (sept, 1H, *J* = 8.2 Hz, $CH(CH_3)_2$), 2.56 (t, 6H, *J* = 3.0 Hz, CH_2), 2.96 (br, 1H, CH_2OH), 3.24 (q, 1H, *J* = 5.6 Hz, C*H*), 3.89 (m, 2H, CH_2OH), 6.82 (t, 1H, *J* = 4.8 Hz, Ar*H*), 7.09 (d, 1H, *J* = 4.8 Hz, Ar*H*), 8.34 (s, 1H, -C*H*=N) ppm. MS (FAB): *m/z* 556 [Ru(κ^2-N,O-**L3***)$_2$(NO)Cl$_3$]$^+$, 521 [Ru(κ^2-N,O-**L3***)$_2$(NO)Cl$_2$]$^+$, 486 [Ru(κ^2-N,O-