Ruthenium(II) Complexes with NS_2 Pyridine-Based Dithia-Containing Ligands. Proposed Possible Structural Isomers and X-ray Confirmation of Their Existence

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Ligands **L*X*** of the type NS_2 with *S*-aryl and *S*-alkyl substituents which incorporate the unit 2,6-bis(thiomethyl)-pyridine are produced. Their reaction with $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(DMSO)_4]$ produces the first reported Ru(II)/NS_2 complexes. They present the general formulas $[RuCl_2(\mathbf{L}X)L']$, where $L' = PPh_3$ or DMSO. Several isomers are possible; however, only two have been found in each reaction. The ^1H NMR spectra show that the H_aH_b proton atoms of the pyridine−CH_aH_b−thioether unit are nonisochronous. A $\Delta\delta(H_aH_b)$ value close to 1 ppm is observed for the *cis* complexes while this is smaller for the *trans* analogues. The possible distinct isomers are discussed in terms of steric effects. It is hypothesized that the *trans-dl*, the *trans-meso*, and the *cis-meso-E* would be the structures more favored. Those structures have been confirmed by X-ray diffraction analysis of *trans-dl*-$[RuCl_2(\mathbf{L1})(DMSO)]\cdot 0.5MeOH$, *cis*-$[RuCl_2(\mathbf{L5})(PPh_3)]\cdot CH_2Cl_2$, and *trans-meso*-$[RuCl_2(\mathbf{L6})(PPh_3)]\cdot 1.5MeOH$.

Introduction

Tridentate N_3 meridionally coordinating ligands have received great attention in recent years.[1] On the contrary NS_2 pyridine-based dithia-containing ligands, although presenting the same kind of meridional coordination, have been much less studied.[2−8] This type of ligands can be produced by a central pyridine ring bonded to two thioether-containing arms. This coordinating unit is responsible for the formation of complexes with different metals, principally with Cu,[4] Ni,[5] Pd,[6] and Pt[7] and to much less extent with Fe.[8] We have recently shown the singular coordinating ability of NS_2(*S*-aryl) ligands incorporating the moiety 2,6-bis(thiomethyl)pyridine. It has been proven that Pd(II) and Pt(II) induce acidity to the pyridine−thioether bridging $-CH_2$ groups in ligands **L1** and **L3** (see ligands **L1**−**L7** in Scheme 1), providing a route to anionic ligands which are capable of partly compensating the positive charge of the metal M(II).[9,10] A similar situation had been previously suggested with $[Ru(DMSO)_6][BF_4]_2$ and **L1**.[9] There was however a main difference between the Pd(II), Pt(II), and Ru(II) salts. The Ru(II) in $[Ru(DMSO)_6][BF_4]_2$ does not have anionic coordinating ligands, while these are present in the Pd(II) and Pt(II) sources, $[PdCl_2(CH_3CN)_2]$ and $[NH_4]_2[PtCl_4]$, respectively.

† On the occasion of the 80th birthday of our teacher Prof. Heribert Barrera i Costa, in recognition of his outstanding personal and professional merits.

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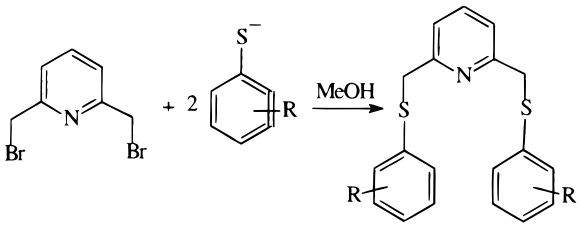
Scheme 1. Synthetic Procedure To Yield the Ligands **L*X*** (**LX** = **L1**−**L7**; o = Ortho, m = Meta, and p = Para Positions)



R = (o) -COOMe L1
(m) -COOMe L2
(p) -COOMe L3
(p) -OMe L4
-H L5
(p) -Cl L6
(p) -NO_2 L7

Thus, it was important to find the role of these ligands. Besides, no structural information about Ru complexes with the NS_2(*S*-aryl) or -(*S*-alkyl) coordinating unit was available. This prompted us to study the coordinating behavior of these ligands and the physical characteristics of the resulting Ru(II) complexes. Ligands **L1**−**L8** (**L8** being an NS_2(*S*-alkyl) derivative; see Figure 1) were chosen to permit adequate comparison. Ligands **L1**−**L3** are chemically very similar although they present clear differences due to the $-CO_2Me$ group disposition in the aromatic ring. On the contrary ligands **L4**−**L7** are structurally very similar but with distinct electronic properties. This work also aims at comparing NS_2(*S*-aryl), **L1**−**L7**, with NS_2(*S*-alkyl), **L8**, toward Ru(II) coordination and to see the influence of ancillary ligands. The preparation of the complexes along with the nature and identification of the possible isomers is described in this paper.

Experimental Section

Materials and Methods. 2,6-Bis(bromomethyl)pyridine was synthesized as reported.[11] The 3- and 4-mercaptobenzoic methyl esters were synthesized as reported,[12] and the other mercapto derivatives were used as received. 2,6-Bis(((2′-(methoxycarbonyl)phenyl)thio)methyl)-pyridine (**L1**), 2,6-bis((phenylthio)methyl)pyridine (**L5**) and 2,6-bis-(((4′-chlorophenyl)thio)methyl)pyridine (**L6**) were synthesized as described previously.[13] 2,6-Bis((ethylthio)methyl)pyridine (**L8**) was synthesized as reported.[14] The starting ruthenium complexes $[RuCl_2(PPh_3)_3]$[15] and $[Ru\ Cl_2(DMSO)_4]$[16] were synthesized as reported.

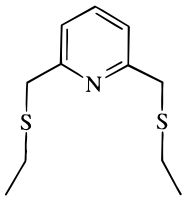


Figure 1. Molecular drawing of **L8**.

Microanalyses were performed using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker spectrometers; chemical shifts are given in ppm. Chemical shift values for ^1H NMR spectra were referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for $^{31}P\{^1H\}$ NMR spectra were referenced relative to external 85% H_3PO_4.

All ligands and complexes were synthesized under a dinitrogen atmosphere by employing Schlenk techniques. Solvents were placed under vacuum to eliminate dissolved oxygen.

2,6-Bis(((3′-(methoxycarbonyl)phenyl)thio)methyl)pyridine (L2). To a stirred solution of sodium metal (0.32 g, 13 mmol) in methanol (25 mL) was added 3-mercaptobenzoic methyl ester, and the mixture was stirred for a further 10 min. The solution was then added to another one of 2,6-bis(bromomethyl)pyridine (1.73 g, 6.5 mmol) in methanol (25 mL). The mixture was heated at 30−35 °C for 30 min and then cooled to room temperature. The methanol was evaporated under reduced pressure. The resulting yellow residue was extracted with diethyl ether (50 mL), and the organic layer was washed twice with distilled water (2 × 50 mL), dried ($MgSO_4$), and vacuum evaporated to afford **L2** as an oil which solidified upon contact with petroleum ether at 5 °C. Yield: 2.12 g (74%). FTIR (KBr): ν(C═O) 1718 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.89 (s, 6H, COOCH_3), 4.29 (s, 4H, py−CH_2−S), 7.19 (d, ^3J(H,H) = 7.9 Hz, 2H, H_{3py}), 7.29 (dd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 7.9 Hz, 2H, H_{5Ph}), 7.47 (br d, ^3J(H,H) = 7.9 Hz, 2H, H_{6Ph}), 7.54 (t, ^3J(H,H) = 7.9 Hz, 1H, H_{4py}), 7.82 (br d, ^3J(H,H) = 7.6 Hz, 2H, H_{4Ph}), 8.04 (br s, 2H, H_{2Ph}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 39.93 (s, py−CH_2−S), 52.24 (s, COOCH_3), 121.48−156.94 (C_{aryl}), 166.51 (s, C$OOCH_3$). Anal. Calcd for $C_{23}H_{21}NO_4S_2$: C, 62.85; H, 4.82; N, 3.19; S, 14.59. Found: C, 62.70; H, 4.86; N, 3.22; S, 13.98.

2,6-Bis(((4′-(methoxycarbonyl)phenyl)thio)methyl)pyridine (L3). **L3** was prepared by following the procedure for **L2**, using 4-mercaptobenzoic methyl ester (1.91 g, 11.4 mmol), sodium metal (0.26 g, 11.4 mmol), and 2,6-bis(bromomethyl)pyridine (1.51 g, 5.7 mmol). Yield: 1.61 g (64%). FTIR (KBr): ν(C═O) 1708 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.88 (s, 6H, COOCH_3), 4.32 (s, 4H, py−CH_2−S), 7.27 (d, ^3J(H,H) = 7.4 Hz, 2H, H_{3py}), 7.35 (d, ^3J(H,H) = 7.8 Hz, 4H, H_{2Ph}), 7.56 (t, ^3J(H,H) = 7.4 Hz, 1H, H_{4py}), 7.87 (d, ^3J(H,H) = 7.8 Hz, 4H, H_{3Ph}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.5 MHz): δ 38.62 (s, py−CH_2−S), 52.02 (s, COOCH_3), 121.42−156.62 (C_{aryl}), 166.65 (s, C$OOCH_3$). Anal. Calcd for $C_{23}H_{21}NO_4S_2$: C, 62.85; H, 4.82; N, 3.19; S, 14.59. Found: C, 62.17; H, 4.78; N, 3.07; S, 13.87.

2,6-Bis(((4′-methoxyphenyl)thio)methyl)pyridine (L4). **L4** was prepared by following the procedure for **L2** using 4-methoxybenzenethiol (1.09 g 7.6 mmol), sodium metal (0.17 g, 7.6 mmol), and 2,6-bis(bromomethyl)pyridine (1.01 g, 3.8 mmol). Yield: 1.45 g (88%). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.75 (s, 6H, CH_3−O), 4.15 (s, 4H, py−CH_2−S), 6.77 (d, ^3J(H,H) = 8.8 Hz, 4H, H_{3Ph}), 7.03 (d, ^3J(H,H)

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= 7.7 Hz, 2H, H_{3py}), 7.24 (d, ^3J(H,H) = 8.8 Hz, 4H, H_{2Ph}), 7.48 (t, ^3J(H,H) = 7.7 Hz, 1H, H_{4py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 41.8 (s, py−*C*H_2−S), 55.27 (s, *C*H_3−O), 114.53−159.24 (C_{aryl}). Anal. Calcd for $C_{21}H_{21}NO_2S_2$: C, 65.77; H, 5.52; N, 3.65; S, 16.72. Found: C, 65.60; H, 5.66; N, 3.62; S, 16.34.

2,6-Bis(((4′-nitrophenyl)thio)methyl)pyridine (L7). To a stirred solution of 98% sodium hydroxide (1.8 g, 45 mmol) in ethanol (200 mL) was added *p*-nitrothiophenol (7.0 g, 45 mmol), and the mixture was heated to reflux for 30 min. After this time the mixture is cooled to 0 °C. Then, a solution of 2,6-bis(bromomethyl)pyridine (5.38 g, 20 mmol) in ethanol (100 mL) was added. After addition, an orange precipitate appeared. The mixture was stirred at 0 °C for 1 h. The precipitate was filtered out, washed with water, redissolved in THF, dried ($MgSO_4$), and vacuum evaporated to afford **L7** as an orange solid. Yield: 4.68 g (56%). ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 4.52 (s, 4H, py−CH_2−S), 7.47 (d, ^3J(H,H) = 7.6 Hz, 2H, H_{3py}), 7.65 (d, ^3J(H,H) = 8.9 Hz, 4H, H_{2Ph}), 7.77 (t, ^3J(H,H) = 7.6 Hz, 1H, H_{4py}), 8.08 (d, ^3J(H,H) = 8.9 Hz, 4H, H_{3Ph}).$^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 400 MHz): δ 37.11 (s, py−*C*H_2−S), 121.46 (s, C_{3py}), 123.26 (s, C_{3Ph}), 126.21 (s, C_{2Ph}), 137.66 (s, C_{4py}), 144.74 and 146.89 (C_{4Ph} and C_{1Ph}), 156.28 (s, C_{2py}). Anal. Calcd for $C_{19}H_{15}N_3O_4S_2$: C, 55.20; H, 3.63; N, 10.17; S, 15.49. Found: C, 55.32; H, 3.78; N, 9.92; S, 15.26.

[$RuCl_2$(L1)(DMSO)]. The ligand **L1** (100 mg, 0.23 mmol) was added to a suspension of [$RuCl_2(DMSO)_4$] (110 mg, 0.23 mmol) in methanol (25 mL). The mixture was heated under reflux for 10 h. The solution was allowed to stand overnight, and a solid was obtained in microcrystalline form, which was filtered out and washed with methanol (1 mL). Yield: 149 mg (94%). FTIR (KBr): ν(C═O) 1721 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1st dias. (60%) 3.95 (s, COOCH_3), 4.41 (d, ^2J(H,H) = 17 Hz, py−C(H_A)(H_B)−S), 5.33 (d, ^2J(H,H) = 17 Hz, py−C(H_A)(H_B)−S), 7.21−8.11 (m, H_{aryl}); δ 2nd dias. (40%) 3.95 (s,COOCH_3), 4.88 (d, ^2J(H,H) = 15 Hz, py−C(H_A)(H_B)−S), 5.10 (d, ^2J(H,H) = 15 Hz, py−C(H_A)(H_B)−S), 7.21−8.11 (m, H_{aryl}). Anal. Calcd for $C_{25}H_{27}Cl_2NO_5RuS_3$: C, 43.54; H, 3.92; N, 2.03; S, 13.93; Cl, 10.30. Found: C, 43.12; H, 3.99; N, 2.00; S, 13.78; Cl, 10.00. Crystals suitable for X-ray diffraction were grown from methanol.

[$RuCl_2$(L2)(PPh_3)]. The ligand **L2** (45 mg, 0.1 mmol) and [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol) were added to a two-necked round-bottom flask. To this mixture, 5 mL of toluene was added, and the solution was heated under reflux for 1 h. After this time, the orange solid was filtered out, washed with diethyl ether and ethanol, and dried under vacuum. Yield: 40 mg (46%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1st dias. (63%) 3.87 (s, COOCH_3), 4.39 (br d, ^2J(H,H) = 16.5 Hz, py−C(H_A)(H_B)−S), 5.53 (br d, ^2J(H,H) = 16.5 Hz, py−C(H_A)(H_B)−S), 7.21−7.86 (m, H_{aryl}); δ 2nd dias. (37%) 3.87 (s, COOCH_3), 5.00 (br d, ^2J(H,H) = 15.4 Hz, py−C(H_A)(H_B)−S), 5.07 (br d, ^2J(H,H) = 15.4 Hz, py−C(H_A)(H_B)−S), 7.21−7.86 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 51.93 (s, py−(*C*H_2−S)$_A$), 52.52 (s, py−(*C*H_2−S)$_B$), 52.17 (s, COO*C*H_3), 120.51−161.44 (C_{aryl}), 166.06 (s, *C*OOCH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 42.70, 46.28 (s, *P*Ph_3). Anal. Calcd for $C_{41}H_{36}Cl_2NO_4PRuS_2$: C, 56.36; H, 4.15; N, 1.60; S, 7.34. Found: C, 54.93; H, 4.14; N, 1.61; S, 6.87.

[$RuCl_2$(L3)(PPh_3)]. [$RuCl_2$(**L3**)(PPh_3)] was prepared by following the procedure for [$RuCl_2$(**L2**)(PPh_3)] using **L3** (45 mg, 0.1 mmol) and [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol). Yield: 67 mg (77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1st dias. (45%) 3.89 (s, COOCH_3), 4.42 (br d, ^2J(H,H) = 13.6 Hz, py−C(H_A)(H_B)−S), 5.53 (br d, ^2J(H,H) = 13.6 Hz, py−C(H_A)(H_B)−S), 7.01−7.80 (m, H_{aryl}); δ 2nd dias. (55%) 3.89 (s, COOCH_3), 5.04 (br s, py−CH_2−S), 7.01−7.80 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 51.56 (s, py−(*C*H_2−S)$_A$), 51.86 (s, py−(*C*H_2−S)$_B$), 52.15 (s, COO*C*H_3), 120.42−134.68 (C_{aryl}), 166.39 (s, *C*OOCH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 42.27, 45.89 (s, *P*Ph_3). Anal. Calcd for $C_{41}H_{36}Cl_2NO_4PRuS_2$: C, 56.36; H, 4.15; N, 1.60; S, 7.34. Found: C, 56.60; H, 4.34; N, 1.54; S, 7.10.

[$RuCl_2$(L4)(PPh_3)]·2H_2O. [$RuCl_2$(**L4**)(PPh_3)]·2H_2O was prepared by following the procedure for [$RuCl_2$(**L2**)(PPh_3)] using **L4** (38 mg, 0.1 mmol) and [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol). A brown-green solid was obtained. Yield: 34 mg (42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1st dias. (50%) 1.59 (br s, H_2O), 3.75 (s, CH_3−O), 4.29 (br d, ^2J(H,H) = 16.1 Hz, py−C(H_A)(H_B)−S), 5.49 (br d, ^2J(H,H) = 16.1 Hz, py−C(H_A)(H_B)−S), 6.53−7.68 (m, H_{aryl}); δ 2nd (50%) 1.59 (br s, H_2O), 3.75 (s, CH_3−O), 4.90 (br d, ^2J(H,H) = 14.4 Hz, py−C(H_A)-(H_B)−S), 4.99 (br d, ^2J(H,H) = 14.4 Hz, py−C(H_A)(H_B)−S), 6.53−7.68 (m, H_{aryl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 44.70, 47.32 (s, *P*Ph_3). Anal. Calcd for $C_{39}H_{40}Cl_2NO_4PRuS_2$: C, 54.90; H, 4.72; N, 1.64; S, 7.51. Found: C, 55.28; H, 4.30; N, 1.64; S, 7.05.

[$RuCl_2$(L4)(DMSO)]. [$RuCl_2$(**L4**)(DMSO)] was prepared by following the procedure for [$RuCl_2$(**L2**)(PPh_3)] using **L4** (76 mg, 0.1 mmol) and [$RuCl_2(DMSO)_4$] (96 mg, 0.1 mmol). An orange solid was obtained. Yield: 51 mg (75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1st dias. (26%) 3.02 (s, (CH_3)$_2$SO), 3.79 (s, CH_3−O), 4.96 (s, py−CH_2−S), 6.80−7.76 (m, H_{aryl}); δ 2nd dias. (74%) 3.15 (s, (CH_3)(CH$_3$)SO), 3.37 (s, (CH$_3$)(CH_3)SO), 3.77 (s, CH_3−O), 4.47 (d, ^2J(H,H) = 16.6 Hz, py−C(H_A)(H_B)−S), 5.32 (d, ^2J(H,H) = 16.6 Hz, py−C(H_A)(H_B)−S), 6.80−7.76 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 46.41, 46.97 (s, (*C*H_3)$_2$SO), 50.62, 50.84 (s, py−*C*H_2−S), 55.27 (s, *C*H_3−O), 114.41−161.88 (C_{aryl}). Anal. Calcd for $C_{23}H_{27}Cl_2NO_3RuS_3$: C, 43.60; H, 4.30; N, 2.21; S, 15.15. Found: C, 43.20; H, 4.10; N, 2.20; S, 15.40.

[$RuCl_2$(L5)(PPh_3)]·MeOH. The ligand **L5** (34 mg, 0.1 mmol) dissolved in methanol (20 mL) was added to a suspension of [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol) in methanol (20 mL). The mixture was refluxed for 30 min. The hot solution was filtered and then cooled to room temperature. After slow and partial evaporation of the solvent, a crystalline orange precipitate was obtained. Yield: 58 mg (71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1st dias. (44%) 3.48 (s, CH_3−OH), 4.34 (br d, ^2J(H,H) = 18.4 Hz, py−C(H_A)(H_B)−S), 5.48 (br d, ^2J(H,H) = 18.4 Hz, py−C(H_A)(H_B)−S), 7.01−7.67 (m, H_{aryl}); δ 2nd (56%) 3.48 (s, CH_3−OH), 4.97 (br s, py−CH_2−S), 7.01−7.67 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 52.25, 52.72 (s, py−*C*H_2−S), 119.96−136.00 (C_{aryl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 44.74, 47.93 (s, *P*Ph_3). Anal. Calcd for $C_{38}H_{36}Cl_2NOPRuS_2$: C, 57.79; H, 4.59; N, 1.77; S, 8.12; Cl, 8.98. Found: C, 57.82; H, 4.39; N, 1.77; S, 8.17; Cl, 9.22. Crystals suitable for X-ray diffraction were grown from dichloromethane/hexane.

[$RuCl_2$(L6)(PPh_3)]·MeOH. [$RuCl_2$(**L6**)(PPh_3)]·MeOH was prepared by following the procedure for [$RuCl_2$(**L5**)(PPh_3)]·MeOH using **L6** (40 mg, 0.1 mmol) and [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol). After slow and partial evaporation of the solvent a crystalline orange precipitate was obtained. Yield: 60 mg (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1st dias. (40%) 3.46 (s, CH_3−OH), 4.31 (br d, ^2J(H,H) = 16.0 Hz, py−C(H_A)(H_B)−S), 5.46 (br d, ^2J(H,H) = 16.0 Hz, py−C(H_A)-(H_B)−S), 6.99−7.97 (m, H_{aryl}); δ 2nd (60%) 3.46 (s, CH_3−OH), 4.90 (br d, ^2J(H,H) = 14.8 Hz, py−C(H_A)(H_B)−S), 5.00 (br d, ^2J(H,H) = 14.8 Hz, py−C(H_A)(H_B)−S), 6.99−7.97 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 52.28, 52.80 (s, py−*C*H_2−S), 120.21−161.40 (C_{aryl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 44.19, 47.40 (s, *P*Ph_3). Anal. Calcd for $C_{38}H_{34}Cl_4NOPRuS_2$: C, 53.15; H, 3.99; N, 1.63; S, 7.47; Cl, 16.50. Found: C, 52.75; H, 3.86; N, 1.62; S, 7.30; Cl, 15.72. Crystals suitable for X-ray diffraction were grown from methanol.

[$RuCl_2$(L7)(PPh_3)]·MeOH. [$RuCl_2$(**L7**)(PPh_3)]·MeOH was prepared following the procedure for [$RuCl_2$(**L5**)(PPh_3)]·MeOH using **L7** (100 mg, 0.2 mmol) and [$RuCl_2(PPh_3)_3$] (25 mg, 0.2 mmol). A brown precipitate was obtained, yield: 42 mg (20%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1st dias. (40%) 3.43 (s, CH_3−OH), 4.44 (br d, ^2J(H,H) = 16.0 Hz, py−C(H_A)(H_B)−S), 5.52 (br d, ^2J(H,H) = 16.0 Hz, py−C(H_A)-(H_B)−S), 6.99−7.97 (m, H_{aryl}); δ 2nd (60%) 3.43 (s, CH_3−OH), 5.01 (br d, ^2J(H,H) = 14.8 Hz, py−C(H_A)(H_B)−S), 5.10 (br d, ^2J(H,H) = 14.8 Hz, py−C(H_A)(H_B)−S), 6.99−7.97 (m, H_{aryl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ: 41.90, 45.92 (s, *P*Ph_3). Anal. Calcd for $C_{38}H_{34}Cl_2N_3O_5PRuS_2$: C, 51.88; H, 3.89; N, 4.77; S, 7.28; Cl, 8.06. Found: C, 52.81; H, 3.69; N, 4.40; S, 6.37; Cl, 8.42.

[$RuCl_2$(L8)(PPh_3)]·MeOH. [$RuCl_2$(**L8**)(PPh_3)]·MeOH was prepared by following the procedure for [$RuCl_2$(**L5**)(PPh_3)]·MeOH using **L8** (23 mg, 0.1 mmol) and [$RuCl_2(PPh_3)_3$] (100 mg, 0.1 mmol). After slow and partial evaporation of the solvent a microcrystalline yellow-orange precipitate was obtained. Yield: 34 mg (48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1st dias. (62%) 1.12 (t, ^3J(H,H) = 6.5 Hz, CH_3−CH$_2$−S), 2.34 (q, ^3J(H,H) = 6.5 Hz, CH$_3$−CH_2−S), 3.47 (s, CH_3−OH), 4.08 (d, ^2J(H,H) = 16.2 Hz, py−C(H_A)(H_B)−S), 5.00 (d, ^2J(H,H) = 16.2 Hz, py−C(H_A)(H_B)−S), 7.26−7.76 (m, H_{aryl}); δ 2nd (38%) 1.05 (t, ^3J(H,H) = 6.5 Hz, CH_3−CH$_2$−S), 2.17 (dq, ^2J(H,H) = 13.4

Table 1. Crystallographic Data for *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH, *cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2, and *trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH

compd	*trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH	*cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2	*trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH
chem formula	$C_{25.5}H_{29}Cl_2NO_{5.5}RuS_3$	$C_{38}H_{34}Cl_4NPRuS_2$	$C_{38.5}H_{36}Cl_4NO_{1.5}PRuS_2$
fw	595.2	842.62	874.64
T, °C	20	20	23
λ, Å	0.710 69	0.710 69	0.710 69
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	36.320(4)	10.078(3)	16.517(2)
b, Å	10.744(3)	11.458(2)	12.987(3)
c, Å	15.781(2)	31.886(3)	19.650(2)
β, deg	110.06(1)	96.72(1)	110.332(8)
V, Å^3	5785(2)	3657(1)	3952(1)
Z	8	4	4
d_{calcd}, g cm^{-3}	1.621	1.531	1.470
μ, cm^{-1}	9.82	9.08	8.46
transm coeff	0.907−1.000	0.883−0.998	0.902−1.000
F(000)	2872	1712	1780
goodness-of-fit on F^2	1.057	1.045	0.960
R^a	0.0304	0.0346	0.0563
wR^b	0.0742	0.1007	0.1467

[a] $R = \sum||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Hz, ^3J(H,H) = 6.5 Hz, CH_3−C(H_1)(H_2)−S), 2.68 (dq, ^2J(H,H) = 13.4 Hz, ^3J(H,H) = 6.5 Hz, CH_3−C(H_1)(H_2)−S), 3.47 (s, CH_3−OH), 4.43 (d, ^2J(H,H) = 15.2 Hz, py−C(H_A)(H_B)−S), 4.70 (d, ^2J(H,H) = 15.2 Hz, py−C(H_A)(H_B)−S), 7.26−7.76 (m, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 12.56, 12.72 (s, CH_3−CH_2−S), 28.43, 29.53 (s, CH_3-CH_2−S), 46.11, 47.52 (s, py−CH_2−S), 120.58−161.04 (C_{aryl}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 45.63, 47.03 (s, PPh_3). Anal. Calcd for $C_{30}H_{36}Cl_2NOPRuS_2$: C, 51.94; H, 5.23; N, 2.01; S, 9.24; Cl, 10.22. Found: C, 52.44; H, 5.18; N, 1.99; S, 9.24; Cl, 10.47.

X-ray Studies. Single-crystal data collections for the compounds *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH and *trans-meso*-[$RuCl_2$(**L6**)-(PPh_3)]·1.5MeOH were carried out on a Rigaku AFC-5S diffractometer, while that for the *cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2 were made with a CAD4 Enraf-Nonius diffractometer. Single-crystal data collections for each compound were performed at ambient temperature using graphite-monochromatized Mo Kα radiation. A total of 4614, 4448, and 4616 observed reflections [$I > 2\sigma(I)$] were collected by the $\omega/2\theta$ scan mode for *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH, *cis*-[$RuCl_2$(**L5**)(PPh_3)]·-CH_2Cl_2, and *trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH, respectively.

The structures were solved by direct methods by using the SHELX-90 program[17] and refined on F^2 by the SHELXL-93 program.[18] For *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms, except those of disordered methanol molecule, were placed at their calculated positions. Hydrogen atoms of the methanol molecule could not be reliably positioned. For *cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at their calculated positions. The asymmetric unit of *trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH contains disordered methanol molecules in three neighboring positions. Non-hydrogen atoms of the methanol molecules were refined with isotropic displacement parameters, but hydrogen atoms could not be reliably positioned. The remaining non-hydrogen atoms were refined with anisotropic displacement parameters, and the remaining hydrogen atoms were placed at their calculated positions. Crystallographic data and structure refinement parameters are presented in Table 1, and selected bond lengths and angles of the three complexes in Table 2.

Results

The reaction of 2,6-bis(bromomethyl)pyridine with thiophenol derivatives 3-(methoxycarbonyl)thiophenol, 4-(methoxycarbonyl)thiophenol, 4-methoxythiophenol, and 4-nitrothiophenol in NaOH/MeOH yields podand ligands containing the coordinating group NS_2(*S*-aryl): 2,6-bis(((3-methoxycarbonyl)phenyl)thio)-methyl)pyridine (**L2**); 2,6-bis(((4-methoxycarbonyl)phenyl)thio)-methyl)pyridine (**L3**); 2,6-bis(((4-methoxyphenyl)thio)methyl)-pyridine (**L4**); 2,6-bis(((4-nitrophenyl)thio)methyl)pyridine (**L7**). Scheme 1 exemplifies these reactions.

A similar reaction leading to the NS_2(*S*-alkyl)ligand **L8** containing the ethyl group bonded to S (Figure 1) has also been conducted.

The reaction of **L1**−**L8** with [$RuCl_2(PPh_3)_3$] and [$RuCl_2$-$(DMSO)_4$] in a 1:1 molar ratio in methanol or toluene yielded complexes of the stoichiometry [$RuCl_2$(**L*X***)L′] (where **L*X*** = **L1**−**L8** and L′ = PPh_3 or DMSO).

Discussion

2,6-Bis((arylthio)methyl)pyridine is prone to rearrangements when complexed with Pd(II), Pt(II), and presumably Ru(II) metal ions.[9] The factors influencing these rearrangements have not been studied, although it is hypothesized that the ease of allyl formation by the pyridine−CH_2−thioether moiety does facilitate the ligand's rearrangements.[19] For better insight into the chemistry of these NS_2 pyridine-based dithia *S*-aryl- and *S*-alkyl-containing ligands, reactions have been performed with Ru(II) complexes incorporating bulky ligands such as PPh_3 or easily displaced ones such as DMSO. Reactions have been carried out in toluene and methanol. Despite all these differences, the reactions have always led to octahedral Ru(II) complexes where three of the available coordinating positions are occupied by the unaltered NS_2 ligands. The other three positions are occupied by the two coordinating chloride anions, leaving one position for a nonionic ligand. Thus, the complexes present the general formulas [$RuCl_2$(**L*X***)L′].

The methylene py−CH_2−S ^1H NMR resonances, in the free ligands, are found in the range of 4−4.3 ppm as singlets. This implies that at room temperature both −CH_2 proton atoms in the noncomplexed ligands are equivalent. Upon complexation this no longer is so. Typically the ^1H NMR spectrum of the isolated complexes displays a very similar pattern in the region 4−5.5 ppm. Two sets of doublets of doublets are found. The

(17) Sheldrick, G. M. SHELX-90. *Acta Crystallogr.* **1990**, *A46*, 467.
(18) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
(19) Boulton, A. J.; McKillop, A. *Comprehensive heterocyclic chemistry*; Pergamon Press: London, 1984; Vol. 2, p 329.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH, *cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2, and *trans-meso*-[$RuCl_2$(**L6**)(PPh_3]·1.5MeOH

	trans-dl-[$RuCl_2$(**L1**)-(DMSO)]·0.5MeOH	*cis*-[$RuCl_2$(**L5**)-(PPh_3)]·CH_2Cl_2	*trans-meso*[$RuCl_2$(**L6**)-(PPh_3)]·1.5MeOH
Ru−Cl(1)	2.4088(7)	2.427(1)	2.460(1)
Ru−Cl(2)	2.4067(7)	2.465(1)	2.428(1)
Ru−S(1)	2.3527(7)	2.332(1)	2.345(2)
Ru−S(2)	2.3406(7)	2.343(1)	2.316(1)
Ru−S(3)	2.2540(8)		
Ru−P		2.304(1)	2.329(1)
Ru−N	2.079(2)	2.056(3)	2.103(4)
Cl(1)−Ru-Cl(2)	177.55(3)	90.21(4)	171.52(4)
Cl(1)−Ru-N	88.45(6)	173.23(9)	87.6(1)
Cl(2)−Ru-N	89.21(6)	84.8(1)	84.7(1)
S(1)−Ru−S(2)	167.68(2)	164.66(4)	161.85(5)
S(1)−Ru-N	83.82(6)	83.8(1)	82.4(1)
S(2)−Ru-N	83.89(6)	81.12(9)	81.1(1)
S(3)−Ru-N	174.44(6)		
P−Ru−N		98.50(9)	178.9(1)
N−Ru−S(1)−C(7)	−22.1(1)	−23.1(2)	−20.7(2)
N−Ru−S(2)−C(13)	−21.1(1)	−29.8(2)	−29.8(2)
N−Ru−S(1)−C(1)	82.7(1)	85.3(2)	88.1(2)
N−Ru−S(2)−C(14)	84.8(1)	−135.6(2)	−136.4(2)
C(1)−S(1)-C(7)−C(8)	−85.3(2)	−84.7(4)	−87.2(5)
C(14)−S(2)-C(13)−C(12)	−82.0(2)	161.9(3)	163.9(4)
S(3)−Ru−S(1)−C(1)	−101.1(1)		
S(3)−Ru−S(2)−C(14)	−91.31(9)		
P−Ru−S(1)−C(1)		−176.4(2)	−92.9(2)
P−Ru−S(2)−C(14)		125.4(2)	44.5(2)

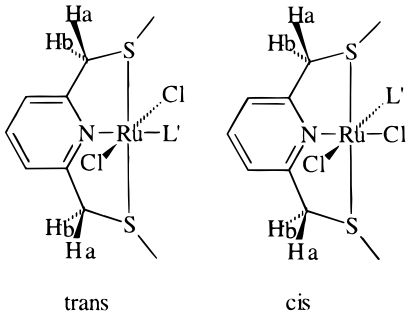

Figure 2. Schematic drawing of the *cis* and *trans* isomers of [$RuCl_2$-(LX)(L)].

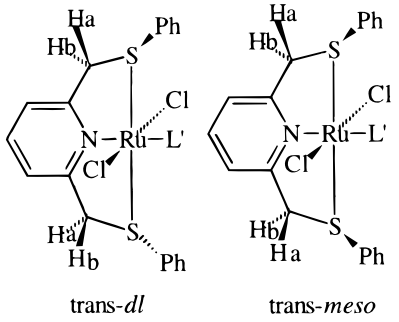

Figure 3. Schematic drawing of the *trans-meso* and *trans-dl* isomers of [$RuCl_2$(LX)(L)].

outer doublet of doublets in the region show a similar pattern, as does the inner set. Both can be interpreted as AB systems. The total integration of the zone agrees well with the other zones in the spectrum. Consequently, the ^{1}H NMR spectra can be interpreted as being the result of two isomers, whose pyridine−CH_aH_b−thioether protons are chemically nonequivalent producing a geminal coupling between them.[20] The graphical interpretation is given in Figure 2.

If a room-temperature fast thioether inversion was considered for the *trans* complex, the four methylene protons in pyridine−CH_aH_b−thioether would be equivalent and only one resonance would be found in the spectra.[21] On the other hand, nonisochronous CH_aH_b would always be expected for the *cis* species. The number of resonances found in the $^{13}C\{^1H\}$ NMR spectra at the $-CH_2-$ region, near 52 ppm in the complexes, is two, and they do not have equal intensity. This confirms the existence of only two isomers in solution and requires that thioether inversion[22] does not take place at room temperature in these ruthenium complexes. The interpretation for the *trans*-[$RuCl_2$(**L*X***)L′] isomer requires a noninversion at the thioether to understand the ^{1}H NMR.[22] Due to the relative disposition of the −S substituents two isomers would be possible, the *trans-meso* and the *trans-dl*, both indicated in Figure 3. The wide shape of the ^{1}H NMR resonances points out that in most cases both isomers *trans-dl* and *trans-meso* coexist in solution.

A similar reasoning could be followed for the *cis* isomer; however, in this case the number of possible isomers is higher since one *cis-dl* and two *cis-meso* species designated *Z* and *E*, in similarity to the alkene terminology, could be formed (see Figure 4). In this case, however, only one is present in solution.

The four methylene protons are nonequivalent at the *cis-dl* form; thus, four sets of groups of resonances would be expected in its spectrum. As indicated, this is not the case, so compound *cis-dl* is not present. However, some hints can be drawn about the nonexistence of this compound. The *cis-dl* structure implies that one substituent on S and the bulky ancillary ligand point to the same direction. This situation produces an sterically crowded region which should not be thermodynamically favor-

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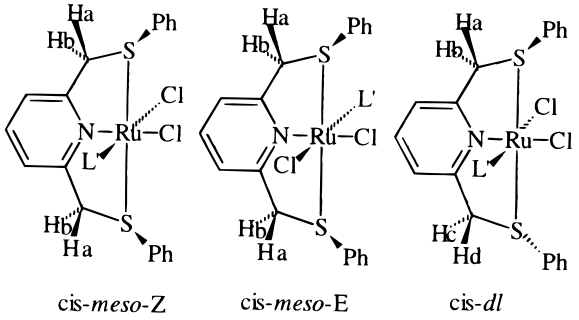

Figure 4. Schematic drawing of the *cis-dl*, *cis-meso-Z*, and *cis-meso-E* isomers of $[RuCl_2(LX)(L)]$.

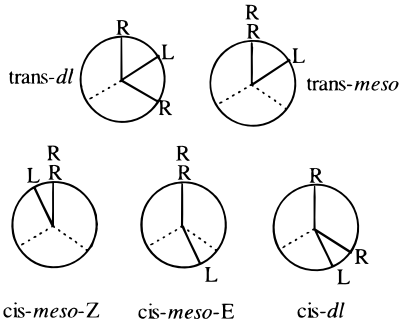

Figure 5. Watch circle representations from the S−Ru−S axis of the different isomers (R = Ph; L = PPh_3 or DMSO).

able. If this reasoning is followed, several of the possible isomers drawn earlier could be eliminated. To do so, Figure 5 is more suitable. The watch circles are drawn focusing at the axis S−Ru−S and considering that the NS_2C_2Ru atoms lie on one plane. In solution, this is most probably so, due to averaging of the $-CH_2$ positions which are moving up and down the plane defined by the NS_2Ru atoms. In the solid state, however, the structures would slightly differ from those because the $-CH_2$ groups would be quenched to get the lowest energy conformers. If one views the molecule through the axis S−Ru−S, the substituents on S are at 120° intervals, while these are at 90° on Ru. Steric repulsions between both S-substituents are considered negligible, while those between S−R and L are considered responsible for the type of isomer produced. Then the *cis-meso-Z* isomer, where L interacts with both S−R substituents in a dihedral angle of 30°, will be most unfavorable.

A second 30° interaction is found in *cis-dl* which provided the basis for this discussion. On the other hand, the most favorable arrangement seems to be provided by *the cis-meso-E*, where a repulsive dihedral angle of 150° is proposed. The two *trans* isomers display repulsive dihedral angles of 60°; thus, both should have similar steric repulsions and both should, in principle, exist. According to this reasoning, if three species are found in the mixture, those should be, in principle, *cis-meso-E* and both *trans* species. Besides, if that was the only reason, the *cis* isomer should be produced in larger quantities.

As indicated in the experimental section, for NS_2(*S*-aryl) complexes a $\Delta\delta(H_aH_b)$ close to 1.1 ppm is found in one isomer while the second isomer has a $\Delta\delta(H_aH_b)$ value close to 0.1 ppm.

The complex $[RuCl_2(\mathbf{L8})L']$ (**L8** = NS_2(*S*-ethyl)) was synthesized with the aim of discerning the *S*-aryl *vs S*-alkyl influence on the $\delta(H_a)$ and $\delta(H_b)$ values. In this complex, two isomers were also found, and the $\Delta\delta(H_aH_b)$ values were comparable to those described earlier. One $\Delta\delta(H_aH_b)$ was smaller, 0.9 ppm, while the second one was slightly higher, 0.3 ppm, as compared to the *S*-aryl compounds. That permitted to conclude that the influence of the S-substituent was not the dominant factor affecting the CH_aH_b ^1H NMR chemical shifts.

Table 3. $\Delta\delta(H_aH_b)$ Observed Values for *Trans* and *Cis* Isomers and Their Ratio in Solution

complex	$\Delta\delta$ *cis*	% *cis*	$\Delta\delta$ *trans*	% *trans*
$[RuCl_2(\mathbf{L2})(PPh_3)]$	1.14	63	0.07	37
$[RuCl_2(\mathbf{L3})(PPh_3)]$	1.11	45	∼0	55
$[RuCl_2(\mathbf{L4})(PPh_3)]$	1.20	50	0.09	50
$[RuCl_2(\mathbf{L4})(DMSO)]$	0.85	74	0	26
$[RuCl_2(\mathbf{L1})(DMSO)]$	0.92	60	0.22	40
$[RuCl_2(\mathbf{L5})(PPh_3)]$	1.14	44	∼0	56
$[RuCl_2(\mathbf{L6})(PPh_3)]$	1.15	40	0.1	60
$[RuCl_2(\mathbf{L7})(PPh_3)]$	1.08	40	0.09	60
$[RuCl_2(\mathbf{L8})(PPh_3)]$	0.92	62	0.27	38

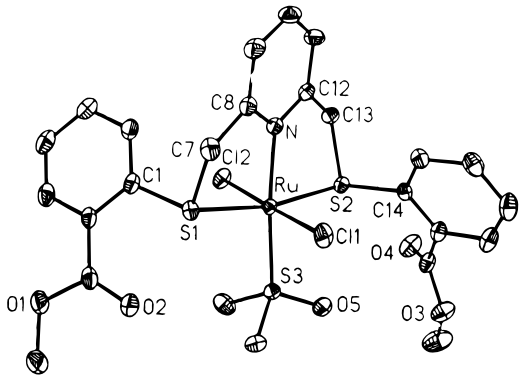

Figure 6. ORTEP plot of complex unit of *trans-dl*-$[RuCl_2(L1)(DMSO)]\cdot 0.5MeOH$ showing 30% ellipsoids. Hydrogen atoms are omitted for clarity.

The geometrical disposition of the chloride ions is the determining factor in the CH_aH_b ^1H NMR chemical shifts difference. When both chloride ions are *trans* to each other, their influence on each CH_aH_b is comparable, producing small $\Delta\delta(H_aH_b)$ values.[23] On the contrary when the relative chloride disposition is *cis*, the CH_aH_b chemical shifts are affected unevenly, producing large $\Delta\delta(H_aH_b)$ values.

This permits us to conclude that the larger $\Delta\delta(H_aH_b)$ values correspond to the *cis* complex and the lower $\Delta\delta(H_aH_b)$ values correspond to the *trans* complex. Table 3 provides a list of the $\Delta\delta(H_aH_b)$ values found, along with the ratio of both isomers in solution.

Obviously, the different natures of the S-substituents will induce variation on the ratios of the *cis vs* the *trans* substituents, but in general, the steric repulsive effect described earlier seems to afford a general understanding of the possible isomers to be expected in these NS_2 derivatives.

Structural work was necessary to support this discussion. Crystals structures of each of the three types of isomers were produced.

Crystal Structure Description. Attempts to grow crystals were made in reactions where **L*X*** or the ancillary ligands were different, in the hope of finding distinct isomers. Crystals where obtained in the reactions leading to $[RuCl_2(\mathbf{L1})(DMSO)]$ (Figure 6), $[RuCl_2(\mathbf{L5})(PPh_3)]$ (Figure 7), and $[RuCl_2(\mathbf{L6})(PPh_3)]$ (Figure 8). The studied compounds revealed three isomers which surprisingly corresponded to the three distinct isomers proposed in the former discussion. The crystals corresponded to *trans-dl*-$[RuCl_2(\mathbf{L1})(DMSO)]\cdot 0.5MeOH$, *cis*-$[RuCl_2(\mathbf{L5})(PPh_3)]\cdot CH_2Cl_2$, and *trans-meso*-$[RuCl_2(\mathbf{L6})(PPh_3)]\cdot 1.5MeOH$. In each compound the metal assumes a distorted octahedral coordination

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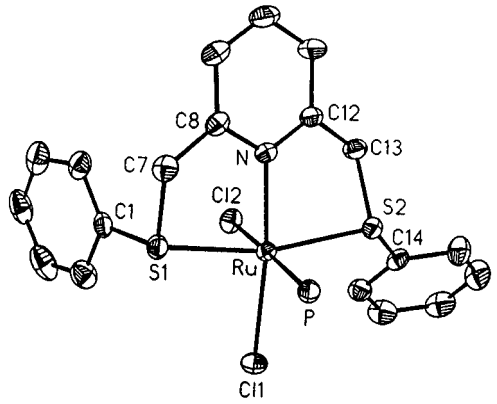

Figure 7. ORTEP plot of complex unit of *cis*-[$RuCl_2$(L5)(PPh_3)]·CH_2Cl_2 showing 30% ellipsoids. The phenyl groups of PPh_3 and hydrogen atoms are omitted for clarity.

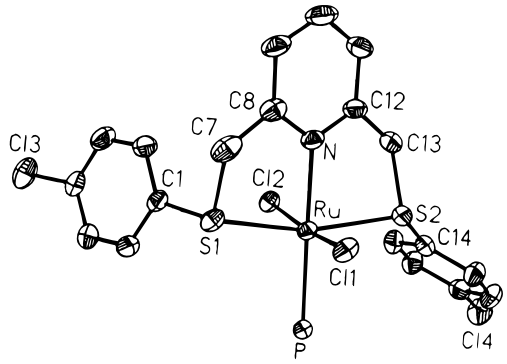

Figure 8. ORTEP plot of complex unit of *trans-meso*-[$RuCl_2$(L6)(PPh_3)]·1.5MeOH showing 30% ellipsoids. The phenyl groups of PPh_3 and hydrogen atoms are omitted for clarity.

sphere and the nonaltered ligand **L*X*** coordinates tridentately via the two S atoms and the N atom of pyridine ring to Ru(II). The remaining three coordination positions are occupied by two chloride ions and the S atom of DMSO or P atom of PPh_3. In addition to the isomerism and differences in the coordination spheres, the most interesting point about the structures is the distinct conformation of the **L*X*** ligands.

The pyridine ring and the plane through the atoms Ru, S(1), S(2), and N are not parallel in any of the three complexes. The pyridine ring is rotated with respect to the two "substituent arms" so that C(7) and C(13) are on the opposite sides of the NS_2Ru plane deviating from it by $\pm 0.66-0.91$ Å. In *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH the phenyl rings are oriented toward opposite sides of the NS_2Ru plane, while in *cis*-[$RuCl_2$(**L5**)(PPh_3)]·CH_2Cl_2 and *trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH the rings occupy the same side of the plane. In the *trans-dl*-complex each methylene carbon is on the opposite side of the plane as is the neighboring phenyl group. In the *trans-meso* and *cis* complexes C(1) and C(7) atoms are on opposite sides of the RuS_2N plane, but the C(13) and C(14) atoms lie on the same side of the plane. These differences can be clearly seen from the torsion angle values listed in Table 2, e.g. for N−Ru−S(1)−C(1) and N−Ru−S(2)−C(14) angle values near 85° (gauche conformation) are obtained when the methylene carbon and its neighboring phenyl group lie on different sides of the NS_2Ru plane, while the values are ca. −136° (*trans* conformation) when the methylene carbon and its neighboring phenyl group lie on the same side of the NS_2Ru plane. The structure with all-*trans* conformation was not found.

Conclusions

The steric repulsive effect described in this report appears as the main one responsible for the synthesis of *trans-dl*, *trans-meso*, and *cis-meso-E* species and not *cis-dl* or *cis-meso-E* isomers. It appears that the nature of the ancillary ligands or the S-substituent does not determine the kind of isomer produced.

The geometrical disposition of the chloride ions but not the S-substituent is the determining factor on the CH_aH_b ^1H NMR chemical shifts. The larger $\Delta\delta(H_aH_b)$ values close to 1 ppm correspond to the *cis* complex. Values close to $\Delta\delta(H_aH_b) = 0.1$ ppm are found for the *trans* isomer.

Although a rearrangement of ligand **L1** in the complexation reaction with [$RuCl_2(PPh_3)_3$] or [$RuCl_2(DMSO)_4$] to an anionic one could be expected, as it occurred with **L1** and [$Ru(DMSO)_6$][(BF_4)]$_2$, this has not taken place. This rearrangement was not necessary for [$RuCl_2(PPh_3)_3$] or [$RuCl_2(DMSO)_4$] probably because anionic coordinating ligands were already present.

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Supporting Information Available: Tables listing crystallographic data, atomic positional and thermal displacement parameters, and bond distances and angles for *trans-dl*-[$RuCl_2$(**L1**)(DMSO)]·0.5MeOH, *cis*-[$RuCL_2$(**L5**)(PPh_3)]·CH_2Cl_2, and *trans-meso*-[$RuCl_2$(**L6**)(PPh_3)]·1.5MeOH (29 pages). Ordering information is given on any current masthead page.

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