Comparative Study of NS_2(*S*-aryl) Pyridine-Based Dithia-Containing Ligands with Different Substituent Groups. Reactivity toward Cu(II) and Ru(II)

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Ligands **L*X*** of the type NS_2 with *S*-aryl substituents which incorporate the unit 2,6-bis(thiomethyl)pyridine modified with functional groups bonded to the aromatic moieties, either on the phenyl or on the pyridine, are produced. Electron-withdrawing groups, 3-chloro and 4-nitro, that reduce the pyridine basicity have been introduced. Methoxy or methoxycarbonyl substituents have been incorporated on the thiophenyl moieties. The comparative results from the reaction of these ligands with $Cu(ClO_4)_2 \cdot 6H_2O$ and $[RuCl_2(PPh_3)_3]$ have revealed that their coordination capacity has not been greatly modified as a result of the introduced groups. Complexes of general formulas $[Cu(\mathbf{LX})][ClO_4]_2$, except for **L5**, and $[RuCl_2(\mathbf{LX})(PPh_3)]$, have been obtained, respectively. The electronic characteristics of these complexes have been studied by cyclic voltammetry experiments. The structures of 2,6-bis[(2′-methoxycarbonyl)phenylthio-methyl]-4-nitropyridine (**L5**) and $[RuCl_2(\mathbf{L5})(PPh_3)] \cdot 2CCl_4$ have been characterized by single-crystal X-ray diffraction methods.

Introduction

Ligands that bind a metal in a 1:1 ratio can be of interest in membrane transport, especially if the ligand is tethered to a support.[1] Tricoordinating ligands are especially attractive because they bind the metal in a bichelating way and do not fulfill all possible coordinating positions, permitting an adequate release of the metal in the stripping solution. In M/H^+ countertransport it is also necessary that the carrier is sensitive to H^+. Thus pyridine derivatives are very promising. The tricoordinating terpy ligand complexed to Ru(II)[2] or Cu(II)[3] has often been used, but it binds to the metals too strongly to be useful in transport. Thioethers are too weak coordinating ligands, although macrocyclic polythioethers form reasonably strong complexes.[4] A ligand combining one base, pyridine, and two thioether units could be a good choice. There are, however, few examples of such a combination of donor atoms.[5] Tricoordinating ligands incorporating the pyridine moiety are usually the result of diimine formation from the readily available 2,6-diacetylpyridine,[6] or the likes. There exist related tricoordinating ligands that incorporate two pyridine moieties joined by nitrogen, e.g., bis(2-pyridylmethyl)amine,[7] or a thioether, e.g., bis(6-methyl-2-pyridylmethyl)thioether.[8] Structurally more related to the work presented in this paper are the non-imine 2,6-pyridine derivatives, e.g., 2,6-[bis(dimethylamino)methyl]-pyridine[9] or bis(*tert*-butylaminomethyl)pyridine.[10]

It has been shown that 2,6-[bis(alkylthio)methyl]pyridine, NS_2(*S*-alkyl), ligands coordinate in a 1:1 ratio to Zn(II), Cu(II), and Ni(II).[11] The ligand preferentially forces the metal to a pentacoordinate environment with the counterions in a cis disposition, although the octahedral arrangement is found in Ru(II) complexes.[5] It was also demonstrated that, when 15-aza-6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene ligand, a NS_2(*S*-alkyl), was used as ionophore in an all-solid-state ISE, some discrimination of Cu(II) vs Ni or Co(II) ($K^{pot}_{Cu,Ni,orCo} = 0.1$)[11] was found. We had also shown that the NS_2(*S*-aryl) ligands coordinate to Cu(II) much more easily than to Zn(II) and Ni(II). Thus a marked difference exists between

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NS_2(*S*-alkyl) and NS_2(*S*-aryl) ligands that had been evidenced in Cu(II) complexes by cyclic voltammetry.[12] The NS_2(*S*-aryl) ligands contain the hard N-donor and soft S-donor atoms but also a π-system able to accept electron density from the metal. An improvement of the ligand π-acidity is accompanied by a reduction of the ligand's σ-donor ability[13] which is related to its basicity. These characteristics prompted us to study further the NS_2(*S*-aryl) ligands, to know to what extent substituents in the pyridine and phenyl groups would modify the σ-donor capacity, i.e., basicity, of the pyridine ring and their electronic properties. In this paper we report the synthesis of this type of NS_2(*S*-aryl) ligand and the reactivity of these ligands toward Cu(II) and Ru(II). The influence of substituent on the pK_A of the ligands and the reduction potentials ($E_{1/2}$) of the Cu(II) and Ru(II) complexes are determined and discussed.

Experimental Section

Materials and Methods. The compounds 4-nitro-2,6-lutidine[14] and 3-chloro-2,6-lutidine[15] were synthesized as reported. 4-Methoxybenzenethiol was commercially available (Aldrich) and used as received. 2,6-Bis[(2′-methoxycarbonyl)phenylthiomethyl]pyridine (**L1**) and its Cu(II) complex, $[Cu(ClO_4)_2(\mathbf{L1})]\cdot H_2O$, were synthesized as described previously.[12] 2,6-Bis[(3′-methoxycarbonyl)phenylthiomethyl]pyridine (**L2**), 2,6-bis[(4′-methoxycarbonyl)phenylthiomethyl]pyridine (**L3**), and 2,6-bis[(4′-methoxyphenyl)thiomethyl]pyridine (**L4**) and their Ru(II) complexes, in the form $[RuCl_2(\mathbf{LX})(PPh_3)]$ (**LX** = **L1**−**L4**), were synthesized as described previously,[16] as was the starting ruthenium complex $[RuCl_2(PPh_3)_3]$.[17]

Microanalyses were performed using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), and $^{31}P\{^1H\}$ NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shift values for ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra are referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for $^{31}P\{^1H\}$ NMR spectra are referenced relative to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million and coupling constants in hertz.

All ligands and complexes were synthesized under a nitrogen atmosphere using Schlenk techniques. Solvents were placed under vacuum to eliminate dissolved oxygen.

Cyclic voltammetric measurements were performed on 1−5 mM solutions of the complexes in dry acetonitrile that contained 0.1 M $[Bu_4N][ClO_4]$ as supporting electrolyte at a rate of 20−100 mV s^{-1}. Two platinum wires, as working electrode and counter electrode, were used with a $Ag/AgCl/Cl^-$ (0.1 M in acetonitrile) electrode as reference. In our experimental setup, the Fc^+/Fc redox couple was found at 0.820 V with reference to $Ag/AgCl/Cl^-$ (0.1 M in acetonitrile). For comparison purposes potential values could be corrected to normal hydrogen electrode (NHE) based on the assumption that $E_{1/2} = 0.340$ V for Fc^+/Fc in acetonitrile.[18] An EG&G Princeton Applied Research potentiostat−galvanostat model 273a was used.

SAFETY NOTE! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Small amounts of perchlorate salts should be prepared and should be handled with great care.

Synthesis of 2,6-Bis(bromomethyl)-4-nitropyridine. A stirred mixture of 4-nitro-2,6-lutidine (2.66 g, 17.5 mmol), *N*-bromosuccinimide (10.17 g, 56.0 mmol), azobis(isobutyronitrile) (75 mg, radical initiator), and benzene (100 mL) was refluxed under light (200 W incandescent bulb) for 12 h. On cooling, a residue formed by succinimide precipitate was filtered and washed with diethyl ether (2 × 50 mL). The benzene and the diethyl ether filtrates were joined and washed with sodium carbonate solution and water. The organic layer was dried over $MgSO_4$ and evaporated under vacuum, and the red oily residue was chromatographed on silica gel using chloroform/hexane (3:2) as mobile phase, $R_f = 0.2$. Yield: 0.54 g, 1.7 mmol (10%). IR (KBr): ν 3085 (C_{aryl}−H), 2924 (C_{alkyl}−H), 1545 (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.63 (s, 4H, py−CH_2−Br), 8.10 (s, 2H, H_{3py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.9 (s, py−CH_2−Br), 115.6 (s, C_{3py}), 155.4 (s, C_{2py}), 159.9 (s, C_{4py}).

Synthesis of 2,6-Bis(bromomethyl)-3-chloropyridine. Following the procedure for 2,6-bis(bromomethyl)-4-nitropyridine, 2,6-bis(bromomethyl)-3-chloropyridine was prepared, using 3-chloro-2,6-lutidine (1.02 g, 7.2 mmol), *N*-bromosuccinimide (3.12 g, 17.3 mmol), azobis(isobutyronitrile) (150 mg, radical initiator), and benzene (100 mL). The mixture was refluxed for 3 h. The final residue was chromatographed on silica gel using chloroform/hexane (1:1) as mobile phase, $R_f = 0.3$. Yield: 0.26 g, 0.9 mmol (12%). IR (KBr): ν 3048 (C_{aryl}−H), 2966 (C_{alkyl}−H), 581 (C−Br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.53 (s, 2H, py−(CH_2)$_a$−Br), 4.68 (s, 2H, py−(CH_2)$_b$−Br), 7.40 (d, ^3J(H,H) = 8.4, 1H, H_{5py}), 7.71 (d, ^3J(H,H) = 8.4, 1H, H_{4py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.7 (s, py−(CH_2)$_a$−Br), 32.5 (s, py−(CH_2)$_b$−Br), 124.5 (s, C_{5py}), 131.0 (s, C_{3py}), 138.6 (s, C_{4py}), 153.5 (s, C_{6py}), 155.2 (s, C_{2py}). Anal. Calcd for $C_7H_6Br_2ClN$: C, 28.06; H, 2.00; N, 4.68. Found: C, 28.34; H, 2.00; N, 4.46.

Synthesis of 2,6-Bis[(2′-methoxycarbonyl)phenylthiomethyl]-4-nitropyridine (L5). To a stirred solution of sodium metal (0.12 g, 5.1 mmol) in methanol (25 mL) was added thiosalicylic methyl ester (0.85 g, 5.1 mmol), and the mixture was stirred for a further 10 min. The solution was then added to another solution of 2,6-bis(bromomethyl)-4-nitropyridine (0.78 g, 2.5 mmol) in methanol (20 mL). After addition, a yellow precipitate appeared. The mixture was stirred at 30−35 °C for 30 min. The precipitate was filtered, washed with methanol (2 × 5 mL) and water (2 × 5 mL), redissolved in chloroform, dried over $MgSO_4$, and vacuum evaporated to afford **L5** as a yellow solid. Yield: 0.86 g, 1.8 mmol (71%). IR (KBr): ν 3023 (C_{aryl}−H), 2952 (C_{alkyl}−H), 1708 (C═O), 1536 (NO_2), 1278, 1250 (C−O−C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 6H, −COOCH_3), 4.16 (s, 4H, py−CH_2−S), 6.92−7.72 (m, 8H, H_{Ph}), 7.80 (s, 2H, H_{3py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 38.5 (s, py−CH_2−S), 52.2 (s, COOCH_3), 114.4−160.4 (C_{aryl}), 166.7 (s, −COOCH$_3$). Anal. Calcd for $C_{23}H_{20}N_2O_6S_2$: C, 56.91; H, 4.12; N, 5.77; S, 13.19. Found: C, 56.95; H, 4.23; N, 5.73; S, 13.19. Crystals suitable for X-ray diffraction were grown from a carbon tetrachloride solution.

Synthesis of 2,6-Bis[(2′-methoxycarbonyl)phenylthiomethyl]-3-chloropyridine (L6). L6 was prepared following the same procedure as for **L5**, using thiosalicylic methyl ester (0.82 g, 4.9 mmol), sodium metal (0.11 g, 4.9 mmol), and 3-chloro-2,6-bis(bromomethyl)pyridine (0.73 g, 2.4 mmol). Yield: 1.01 g, 2.1 mmol (88%). IR (KBr): ν 3062 (C_{aryl}−H), 2953 (C_{alkyl}−H), 1716, 1705 (C═O), 1308, 1274, 1253 (C−O−C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.90 (s, 3H, (COOCH_3)$_A$), 3.91 (s, 3H, (COOCH_3)$_B$), 4.27 (s, 2H, (py−CH_2−S)$_A$), 4.43 (s, 2H, (py−CH_2−S)$_B$), 7.12 (ddd, $^3J(H_{4PhA},H_{3PhA}) = 7.7$ Hz, $^3J(H_{4PhA},H_{5PhA}) = 7.8$ Hz, $^4J(H_{4PhA},H_{6PhA}) = 1.4$, 1H, H_{4PhA}), 7.18 (ddd, $^3J(H_{4PhB},H_{3PhB}) = 7.7$, $^3J(H_{4PhB},H_{5PhB}) = 8.0$ Hz, $^4J(H_{4PhB},H_{6PhB}) = 1.1$, 1H, H_{4PhB}), 7.30 (ddd, $^3J(H_{5PhA},H_{4PhA}) = 7.8$, $^3J(H_{5PhA},H_{6PhA}) = 8.2$, $^4J(H_{5PhA},H_{3PhA}) = 1.7$, 1H, H_{5PhA}), 7.37 (d, $^3J(H_{5py},H_{4py}) = 8.3$, 1H, H_{5py}), 7.38 (dd, $^3J(H_{6PhA},H_{5PhA}) = 8.2$, $^4J(H_{6PhA},H_{4PhA}) = 1.4$, 1H, H_{6PhA}), 7.48 (ddd, $^3J(H_{5PhB},H_{6PhB}) = 8.1$, $^3J(H_{5PhB},H_{4PhB}) = 8.0$, $^4J(H_{5PhB},H_{3PhB}) = 1.7$, 1H, H_{5PhB}), 7.58 (d, $^3J(H_{4py},H_{5py}) = 8.3$, 1H, H_{4py}), 7.78 (dd, $^3J(H_{6PhB},H_{5PhB}) = 8.1$, $^4J(H_{4PhB},H_{6PhB}) = 1.1$, 1H, H_{6PhB}), 7.96 (dd, $^3J(H_{3PhA},H_{4PhA}) = 7.7$, $^4J(H_{3PhA},H_{5PhA}) = 1.7$, 1H, H_{3PhA}), 7.98 (dd, $^3J(H_{3PhB},H_{4PhB}) = 7.7$, $^4J(H_{3PhB},H_{5PhB}) = 1.7$, 1H, H_{3PhB}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.9 (s, (py−CH_2−S)$_A$), 38.1 (s, (py−CH_2−S)$_B$), 52.1 (s, −COOCH_3), 122.9−155.3 (C_{aryl}), 166.9 (s, −COOCH$_3$). Subscript A designates the methylthiophenyl derivative bonded to the pyridine at position 6, and subscript B designates the methylthiophenyl derivative

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bonded to the pyridine at position 2. Anal. Calcd for $C_{23}H_{20}ClNO_4S_2$: C, 58.29; H, 4.22; N, 2.96; S, 13.52. Found: C, 58.34; H, 4.30; N, 2.87; S, 14.05.

Synthesis of 2,6-Bis[(4′-methoxyphenyl)thiomethyl]-3-chloropyridine (L7). L7 was prepared following the same procedure as for **L5**, using 4-methoxybenzenethiol (0.62 g, 4.4 mmol), sodium metal (0.10 g, 4.4 mmol), and 2,6-bis(bromomethyl)-3-chloropyridine (0.65 g, 2.2 mmol). Yield: 0.77 g, 1.8 mmol (84%). IR (KBr): ν 3020(C_{aryl}−H), 2937(C_{alkyl}−H), 1246, 1033 (C−O−C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.77 (s, 3H, (CH_3−O)$_A$), 3.78 (s, 3H, (CH_3−O)$_B$), 4.04 (s, 2H, (py−CH_2−S)$_A$), 4.25 (s, 2H, (py−CH_2−S)$_B$), 6.81 (d, $^3J(H_{3Ph},H_{2Ph}) = 8.8$, 4H, H_{3Ph}), 7.00 (d, $^3J(H_{5py},H_{4py}) = 8.1$, 1H, H_{4py}), 7.25 (d, $^3J(H_{2PhA},H_{3PhA}) = 8.8$, 2H, H_{2PhA}), 7.35 (d, $^3J(H_{2PhB},H_{3PhB}) = 8.8$, 2H, H_{2PhB}), 7.50 (d, $^3J(H_{5py},H_{4py}) = 8.1$, 1H, H_{5py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 40.3 (s, (py−CH_2−S)$_A$), 41.8 (s, (py−CH_2−S)$_B$), 55.3 (s, OCH_3), 114.4−159.4 (C_{aryl}). Subscript A designates the methylthiophenyl derivative bonded to the pyridine at position 6, and subscript B designates the methylthiophenyl derivative bonded to the pyridine at position 2. Anal. Calcd for $C_{21}H_{20}ClNO_2S_2$: C, 60.36; H, 4.79; N, 3.35; S, 15.33. Found: C, 60.51; H, 4.80; N, 3.27; S, 14.93.

Synthesis of [Cu(L2)][ClO$_4$]$_2$·H$_2$O. The ligand **L2** (0.11 g, 0.25 mmol) dissolved in ethyl acetate (4 mL) was added to a solution of $Cu(ClO_4)_2$·$6H_2O$ (0.09 g, 0.25 mmol) in ethyl acetate (2 mL). A violet solid was obtained, which was filtered, washed with ethyl acetate (4 mL), and vacuum-dried. Yield: 0.15 g, 0.21 mmol (86%). IR (KBr): ν 1729 (C═O), 1679 (C═O···H), 1322, 1279 (C−O−C), 1122, 1090 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{23}H_{23}Cl_2CuNO_{13}S_2$: C, 38.36; H, 3.20; N, 1.95; S, 8.89. Found: C, 38.12; H, 3.24; N, 1.81; S, 8.57.

Synthesis of [Cu(L3)][ClO$_4$]$_2$·H$_2$O·$^1/_2$C$_4$H$_8$O$_2$. The procedure is the same as before, using **L3** (0.11 g, 0.25 mmol) and $Cu(ClO_4)_2$·$6H_2O$ (0.09 g, 0.25 mmol). The complex is a brown solid. Yield: 0.10 g, 0.1 mmol (53.1%). IR (KBr): ν 1729 (C═O), 1294, 1287 (C−O−C), 1151, 1118, 1092 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{25}H_{27}Cl_2CuNO_{14}S_2$: C, 39.81; H, 3.58; N, 1.86; S, 8.49. Found: C, 39.46; H, 3.40; N, 2.14; S, 8.77.

Synthesis of [Cu(L4)][ClO$_4$]$_2$. The procedure is the same as before, using **L4** (0.10 g, 0.25 mmol) and $Cu(ClO_4)_2$·$6H_2O$ (0.09 g, 0.25 mmol). The complex is a violet solid. Yield: 0.06 g, 0.09 mmol (37%). IR (KBr): ν 1261, 1180, 1025 (C−O−C), 1115, 1088 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{21}H_{21}Cl_2CuNO_{10}S_2$: C, 39.04; H, 3.25; N, 2.17; S, 9.91. Found: C, 38.87; H, 3.15; N, 2.03; S, 9.56.

Synthesis of [Cu$_2$(L5)$_2$O][ClO$_4$]. The procedure is the same as before, using **L5** (0.12 g, 0.25 mmol) and $Cu(ClO_4)_2$·$6H_2O$ (0.09 g, 0.25 mmol). The complex is a deep blue solid. Yield: 0.13 g, 0.17 mmol (68%). IR (KBr): ν 1704 (C═O), 1542, 1357 (NO_2), 1289, 1258 (C−O−C), 1120, 1110, 1086 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{46}H_{40}Cl_2Cu_2N_4O_{21}S_4$: C, 42.14; H, 3.07; N, 4.27; S, 9.78. Found: C, 42.54; H, 3.10; N, 4.17; S, 9.59.

Synthesis of [Cu(L6)][ClO$_4$]$_2$·H$_2$O. The procedure is as before, using **L6** (0.12 g, 0.25 mmol) and $Cu(ClO_4)_2$·$6H_2O$ (0.09 g, 0.25 mmol). The complex is a violet solid. Yield: 0.16 g, 0.2 mmol (85%). IR (KBr): ν 1710 (C═O), 1260 (C−O−C), 1145, 1118, 1087 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{23}H_{22}Cl_3CuNO_{13}S_2$: C, 36.60; H, 2.92; N, 1.86; S, 8.48. Found: C, 37.00; H, 2.99; N, 1.67; S, 8.51.

Synthesis of [Cu(L7)][ClO$_4$]$_2$·2H$_2$O·$^1/_4$C$_4$H$_8$O$_2$. The procedure is as before, using **L7** and $Cu(ClO_4)_2$·$6H_2O$ in a 0.3 mmol scale. The complex is a deep blue solid. Yield: 0.08 g, 0.1 mmol (42%). IR (KBr): ν 1251 (C−O−C), 1145, 1114, 1092 (ClO_4^-) cm^{-1}. Anal. Calcd for $C_{22}H_{26}Cl_3CuNO_{12.5}S_2$: C, 35.77; H, 3.52; N, 1.90; S, 8.67. Found: C, 35.96; H, 3.76; N, 1.69; S, 8.33.

Synthesis of [RuCl$_2$(L5)(PPh$_3$)]·2CCl$_4$. To a two-necked round bottom flask containing 5 mL of toluene were added 48 mg (0.10 mmol) of ligand **L5** and 100 mg (0.10 mmol) of $[RuCl_2(PPh_3)_3]$. The solution was heated under reflux for 1 h. After concentration to 2 mL, petroleum ether was added until precipitation of a deep blue solid took place. This was filtered, washed with diethyl ether and methanol, and dried under vacuum. Yield: 66 mg, 0.05 mmol (54%). Crystals suitable for X-ray diffraction were grown from carbon tetrachloride. IR (KBr): ν 1713, 1726 (C═O), 1539 (NO_2), 1261 (C−O−C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.69 (s, 6H, COOCH_3), 4.50−5.70 (m, 4H, py−CH_2−S), 7.00−8.30 (m, 25H, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 52.4 (s, py−CH_2−S), 54.6 (s, COOCH_3), 113.0−135.7 (C_{aryl}), 167.0 (s, COOCH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.37 (s, PPh$_3$). Anal. Calcd for $C_{43}H_{35}Cl_{10}N_2O_6PRuS_2$: C, 42.09; H, 2.85; N, 2.28; S, 5.22. Found: C, 41.77; H, 2.86; N, 2.18; S, 4.94.

Synthesis of [RuCl$_2$(L6)(PPh$_3$)]. The ligand **L6** (47 mg, 0.10 mmol) and $[RuCl_2(PPh_3)_3]$ (97 mg, 0.10 mmol) were added to a two-necked round bottom flask. To this mixture was added 12 mL of toluene/diethyl ether (1:5), and the solution was heated under reflux for 1 h. An orange solid appeared, which was filtered, washed with diethyl ether and methanol, and dried under vacuum. Yield: 49 mg, 0.05 mmol (54%). IR (KBr): ν (C═O) 1722 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.67 (s, 3H, COOCH_3), 3.70 (s, 3H, COOCH_3), 4.50−5.50 (m, 4H, py−CH_2−S), 7.00−8.10 (m, 25H, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 52.4 (s, py−CH_2−S), 54.5 (s, COOCH_3), 120.0−136.3 (m, C_{aryl}), 167.0 (s, COOCH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.21 (s, PPh$_3$). Anal. Calcd for $C_{41}H_{35}Cl_3NO_4PRuS_2$: C, 54.22; H, 3.88; N, 1.54; S, 7.06. Found: C, 54.01; H, 3.96; N, 1.54; S, 6.78.

Synthesis of [RuCl$_2$(L7)(PPh$_3$)]·C$_7$H$_8$. The complex [RuCl$_2$(**L7**)(PPh$_3$)]·C_7H_8 was prepared following the same procedure as for [RuCl$_2$(**L6**)(PPh$_3$)] using **L7** (42 mg, 0.1 mmol) and $[RuCl_2(PPh_3)_3]$ (99 mg, 0.1 mmol). Yield: 72 mg, 0.09 mmol (85%). ^1H NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3Ph), 3.76 (s, 6H, CH_3O−), 4.00−5.60 (m, 4H, py−CH_2−S), 6.40−8.00 (m, 30H, H_{aryl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (s, CH$_3$Ph), 51.9 (s, py−CH_2−S), 53.0 (s, py−CH_2−S), 54.0 (s, CH$_3$O−), 55.2 (s, CH$_3$O−), 113.9−140.0 (m, C_{aryl}) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.38 (s, PPh$_3$), 47.41 (s, PPh$_3$). Anal. Calcd for $C_{46}H_{43}Cl_3NO_2PRuS_2$: C, 58.51; H, 4.56; N, 1.48; S, 6.78. Found: C, 58.07; H, 4.68; N, 1.41; S, 6.64.

X-ray Studies. Single-crystal data collections for **L5** and [RuCl$_2$(**L5**)(PPh$_3$)]·$2CCl_4$ were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. Unit cell parameters were determined by least-squares refinement of 20 carefully centered reflections. Data obtained were corrected for Lorentz and polarization effects and for dispersion. Corrections for empirical absorption (ψ scan) were also applied. A total of 2293 and 8858 unique reflections were collected by the $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$) for **L5** and [RuCl$_2$(**L5**)(PPh$_3$)]·$2CCl_4$, respectively.

Both structures were solved by direct methods by using the SHELXS-86 program,[19] and least-squares refinements and all subsequent calculations were performed using the SHELX-97 program system.[20]

For **L5**, non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters.

For [RuCl$_2$(**L5**)(PPh$_3$)]·$2CCl_4$, one of the CCl_4 ions is disordered, showing rotational disorder around the Cl3−C42 bond. Refinement of the disordered chloride ions with isotropic and the rest of the non-hydrogen atoms with anisotropic displacement parameters revealed site occupation parameters 0.588(13) for Cl4a, Cl5a, and Cl6a and 0.412(13) for Cl4b, Cl5b, and Cl6b. These site occupation parameters for the disordered Cl ions were fixed in final refinement, and all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. Crystallographic data and refinement for the compounds are presented in Table 1 and selected bond distances and angles for [RuCl$_2$(**L5**)(PPh$_3$)]·$2CCl_4$ in Table 2.

Results

The ligands presented in this work have in common the NS_2-(*S*-aryl) skeleton, but each one differs from the others in the aromatic ring substituent. Considering substituents on the pyridine, three distinct bis(bromomethyl)pyridine derivatives have been utilized as precursors for the ligand synthesis: 2,6-bis(bromomethyl)pyridine, 2,6-bis(bromomethyl)-3-chloropy-

(19) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.
(20) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for **L5** and $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$

compd	**L5**	$RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$
chem formula	$C_{23}H_{20}N_2O_6S_2$	$C_{43}H_{35}Cl_{10}N_2O_6PRuS_2$
fw	484.53	1226.39
T, °C	21	21
λ, Å	0.71069	0.71069
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	12.072(3)	13.984(3)
b, Å	25.292(5)	15.277(2)
c, Å	7.377(5)	13.508(2)
α, deg	90	94.233(17)
β, deg	90	118.267(13)
γ, deg	90	93.462(18)
V, Å^3	2252.4(17)	2519.7(7)
Z	4	2
D_{calcd}, g cm^{-3}	1.429	1.616
μ, cm^{-1}	2.80	10.04
F(000)	1008	1232
GOF on F^2	1.021	1.013
R1[a] [$I > 2\sigma(I)$]	0.0370	0.0816
wR2[b] [$I > 2\sigma(I)$]	0.0796	0.1697

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

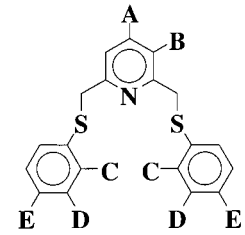
Table 2. Selected Interatomic Distances (Å) and Angles (deg) and Torsion Angles (deg) for $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$

Ru−Cl1	2.432(3)	Ru−S2	2.326(3)
Ru−Cl2	2.424(3)	Ru−P	2.337(3)
Ru−S1	2.360(3)	Ru−N1	2.125(9)
Cl2−Ru−Cl1	170.97(12)	N1−Ru−S1	83.4(3)
S1−Ru−Cl1	79.32(11)	N1−Ru−S2	81.5(3)
S1−Ru−Cl2	100.45(12)	N1−Ru−P	178.7(3)
S2−Ru−S1	158.28(11)		

ridine, and 2,6-bis(bromomethyl)-4-nitropyridine. The last two 2,6-bis(bromomethyl)pyridine derivatives have been synthesized for the first time in this work. Their syntheses are difficult due to the electron poverty of pyridine. Thus, the starting compound for 3-chloro-2,6-lutidine was 2,5-dimethylpyrrole, and the fragment "CCl" was introduced, resulting in 2,6-dimethyl-3-chloropyridine.[15] In the case of nitropyridine it was necessary to synthesize first the pyridine oxide. After introduction of the nitro group, the oxide was removed. The last step to obtain the bis(bromomethyl)pyridine derivatives was the bromination. This was accomplished by using *N*-bromosuccinimide following a similar procedure to this already described.[21] The bis(bromomethyl)pyridine derivatives were obtained in 10% yield, after careful column chromatography separation. The schematic synthetic procedure is shown in Scheme 1.

The reaction of these bis(bromomethyl)pyridine compounds with thiophenol derivatives 2-methoxycarbonylthiophenol (thiosalicylic methyl ester) and 4-methoxybenzenethiol in NaOMe/MeOH yields the podand ligands: 2,6-bis[(2′-(methoxycarbonyl)phenylthiomethyl]-4-nitropyridine (**L5**), 2,6-bis[(2′-(methoxycarbonyl)phenylthiomethyl]-3-chloropyridine (**L6**), and 2,6-bis[(4′-methoxyphenyl)thiomethyl]-3-chloropyridine (**L7**), which were synthesized for the first time in this work. **L5** and **L6** incorporate electron-withdrawing groups both on the pyridine and on the phenyl rings, while **L7** incorporates an electron-withdrawing group on the pyridine ring and an electron-donor group on thiophenyl moieties (−OMe in the para position with respect to S on thiophenyl groups). A schematic representation of ligands **L1**−**L7** is shown in Figure 1.

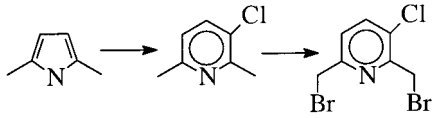
All ligands have their arms equal except for **L6** and **L7**. The



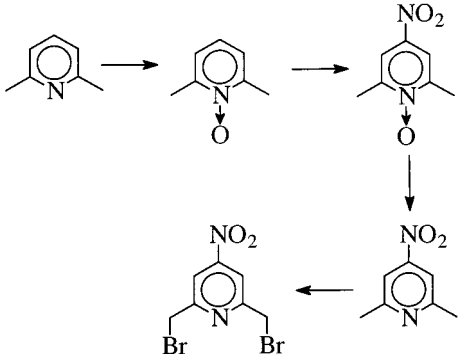
	A	B	C	D	E
L1	H	H	CO_2Me	H	H
L2	H	H	H	CO_2Me	H
L3	H	H	H	H	CO_2Me
L4	H	H	H	H	OMe
L5	NO_2	H	CO_2Me	H	H
L6	H	Cl	CO_2Me	H	H
L7	H	Cl	H	H	OMe

Figure 1. Schematic representation of ligands **L1**−**L7**.

Scheme 1. Synthetic Procedure for the Pyridine Derivatives 2,6-Bis(bromomethyl)-3-chloropyridine and 2,6-Bis(bromomethyl)-4-nitropyridine



2,6-bis(bromo methyl)-3-chloropyridine



2,6-bis(bromomethyl)-4-nitropyridine

inequality is the result of the presence of a Cl atom in the pyridine's 3-position. This produces a chemical shift difference in the corresponding $-CH_2-$ groups both in ^1H and in $^{13}C\{^1H\}$ NMR spectra. The same phenomenon is also observed in the dibromo, 2,6-bis(bromomethyl)-3-chloropyridine, precursor.

Discussion

As it was indicated earlier, the tridentate NS_2(*S*-aryl) pyridine dithia-containing ligands were chosen due to their copper affinity, their ligand/copper ratio in the complexation process, and their ability to coordinate either to copper or to proton through the pyridinic nitrogen, depending on the solution's pH. According to the literature[22] the acidity constant of the tridentate ligand 2,6-bis(methylthiomethyl)pyridine (**L**) and the formation

(21) Offermann, W.; Vögtle, F. *Synthesis* **1977**, 272.

Table 3. Formal Reduction Potentials (vs Ag/AgCl/Cl^- 10^{-1} M in CH_3CN for the Couple Cu(II)/Cu(I)

complex	$E_{1/2}$, V	complex	$E_{1/2}$, V
$[Cu(CH_3CN)_n][ClO_4]_2$[a]	1.47	[Cu(**L6**)][ClO_4]$_2$[b]	1.43
$[Cu_2(\mathbf{L5})_2O][ClO_4]$[a]	1.44	[Cu(**L2**)][ClO_4]$_2$[b]	1.33
[Cu(**L3**)][ClO_4]$_2$[a]	1.40	[Cu(**L7**)][ClO_4]$_2$[b]	1.32
[Cu(**L1**)][ClO_4]$_2$[a]	1.38	[Cu(**L1**)][ClO_4]$_2$[b]	1.32
$[Cu(CH_3CN)_n][ClO_4]_2$[b]	1.42	[Cu(**L4**)][ClO_4]$_2$[b]	1.26

[a] Initial [Cu(II)] = 1.50×10^{-3} M. [b] Initial [Cu(II)] = 5.04×10^{-3} M.

Table 4. Formal Reduction Potentials (vs Ag/AgCl/Cl^- 10^{-1} M in CH_3CN) for the Couple Ru(III)/Ru(II)

complex	$E_{1/2}$, V	complex	$E_{1/2}$, V
[$RuCl_2$(**L2**)(PPh_3)]	1.74	[$RuCl_2$(**L6**)(PPh_3)]	1.76
[$RuCl_2$(**L3**)(PPh_3)]	1.75	[$RuCl_2$(**L7**)(PPh_3)]	1.70
[$RuCl_2$(**L4**)(PPh_3)]	1.66	[$RuCl_2$(**L1**)(PPh_3)]	1.71
[$RuCl_2$(**L5**)(PPh_3)]	1.81		

constant of its Cu(II) complex [Cu**L**(H_2O)]$^{2+}$ are log $K_A = 4.04 \pm 0.04$ and log $K_F = 4.6 \pm 0.1$, respectively. Thus the system appears to be very interesting in copper−proton countertransport in membranes.

In the following discussion the influence on the pK_A of the substituents on the pyridine and/or on the phenyl groups will be discussed along with their influence on the electronic properties. For their study, [Cu(**L*X***)][ClO_4]$_2$ and [$RuCl_2$(**L*X***)(PPh_3)] complexes of **L1**−**L7** have been synthesized. Table 3 presents $E_{1/2}$ for the Cu(II) NS_2(*S*-aryl) complexes. Values ranging from 1.26 to 1.44 V vs Ag/AgCl/Cl^- (0.1 M in acetonitrile) are encountered in [Cu(**L*X***)][ClO_4]$_2$ (**LX** = **L1**−**L7**, for **L5** the formula is [Cu_2(**L5**)$_2$O][ClO_4]). The $\Delta E_{1/2}$ value between the complexes [Cu(**L4**)][ClO_4]$_2$ and [Cu(**L7**)][ClO_4]$_2$ is 60 mV, the more positive being [Cu(**L7**)][ClO_4]$_2$. The ligands **L4** and **L7** are identical except that **L7** has a chlorine atom at the pyridine 3-position. The chlorine makes the electron pair less available for coordination, or lowers the pyridine LUMO, stabilizing more the Cu(I) and consequently increasing $E_{1/2}$ (Cu(II)/Cu(I)).

The same effect is observed comparing **L1** with **L5** and **L6**. The only difference between these ligands is the existence of a nitro group on the pyridine 4-position for **L5** and a chlorine atom on the pyridine 3-position for **L6**. Both ligands, **L5** and **L6**, increase the $E_{1/2}$ (Cu(II)/Cu(I)) with regard to **L1** by 60 and 50 mV, respectively.

Table 4 presents $E_{1/2}$ for the Ru(II) NS_2(*S*-aryl) complexes. Values ranging from 1.66 to 1.81 V are encountered in [$RuCl_2$(**L*X***)(PPh_3)] complexes (**L*X*** = **L1**−**L7**). The same trend observed for the copper complexes is found for the ruthenium ones. Ligands **L5** and **L6** increase the $E_{1/2}$ (Ru(III)/Ru(II)) in 100 and 50 mV respectively with respect to **L1**. The $\Delta E_{1/2}$ between the [$RuCl_2$(**L4**)(PPh_3)] and [$RuCl_2$(**L7**)(PPh_3)] is ca. 40 mV, being the highest for **L7**.

All of the above discussion has been based on the substituents on the pyridine ring; however, the substituents on the phenyl rings can influence the $E_{1/2}$ change. The Ru(II) complex with **L4** has an $E_{1/2} = 1.66$ V. For this example, the substituent on the phenyl ring is −OMe, which has an electron-donor effect (by resonance) since it is placed at the para position with regard to the sulfur atom. When −OMe is replaced by an electron-withdrawing group such as $-CO_2Me$ (**L3**), the reduction potential Ru(III)/Ru(II) increases by 95 mV. The electron-withdrawing groups bonded to the aromatic moieties of NS_2(*S*-aryl) ligands provide an enhanced capacity for stabilizing low-oxidation states.

Table 5. Approximated pK_A Values for **L1**−**L7** (except **L5**)

ligand	**L1**	**L2**	**L3**	**L4**	**L6**	**L7**
pK_A	3.8	3.5	3.6	3.9	3.4	3.4

The approximated pK_A's of ligands **L1**−**L7**, except for **L5**, were calculated following a procedure similar to the one described by Köseoglu et al.[23] The values obtained are presented in Table 5. The values range from 3.4 to 3.9, **L4** being the ligand with the highest basicity or, for this case, the highest σ-donor ability. The pK_A's of **L6**−**L7** are slightly less positive than for **L1**−**L4**, implying that the effect on the pK_A by substitution on the pyridine is stronger than substitution on the thiophenyl group. Ligands **L4** and **L7** only differ by a chlorine atom on pyridine, and pK_A(**L4**) − pK_A(**L7**) = 0.5, but if the substitution is produced on the thiophenyl moiety, ΔpK_A is less pronounced, e.g., pK_A(**L4**) − pK_A(**L3**) = 0.3. This effect is not observed in the $\Delta E_{1/2}$. For instance the **L4** and **L7** ruthenium complexes have an $\Delta E_{1/2} = 40$ mV, the complex with **L7** having the highest $E_{1/2}$ value. For these complexes the difference was on the pyridine moiety, but if the comparison was between ruthenium complexes of **L4** and **L3**, where the substitution was on the phenyl ring, the $\Delta E_{1/2} = 90$ mV. Consequently substitution on pyridine has a greater influence on the pK_A than substitution on the thiophenyl moiety, but the influence on $E_{1/2}$ for both substitutions is comparable.

It results, however, that the $E_{1/2}$ values and the approximated pK_A's for all these ligands are very similar. The electron-withdrawing groups introduced on the aromatic moieties do not considerably alter the electronic properties of the ligand. The effect of introducing electron-withdrawing groups on the pyridine moiety is similar to the effect of introducing these groups on thiophenyl moieties. Thus, the synthetic effort to obtain the trisubstituted pyridines is not compensated by the observed electronic modification of the ligand. Synthetically it is easier to modify the phenyl ring to cause a similar effect. Although some difference in the $E_{1/2}$ values for the couples Cu(II)/Cu(I) and Ru(III)/Ru(II) are observed for **L1** and **L5**, the comparative much larger and difficult synthetic work required to produce substitution on pyridine than on phenyl is not worthwhile considering the minor difference in the results. In reality, the same effects can be produced just modifying adequately the phenyl ring. Also, no major differences are found upon substitution at the ortho, meta, or para positions in the phenyl ring, except for the pK_A, in which case an electron-withdrawing substituent in the meta position produces a lower pK_A.

Crystal Structure Descriptions. To know the geometrical arrangement of the free ligand and its complex, the molecular structures of **L5** and its Ru(II) complex were solved. Figures 2 and 3 show a perspective view of **L5** and [$RuCl_2$(**L5**)(PPh_3)]·$2CCl_4$, respectively.[24]

In **L5** (Figure 2) the substituents connected to C8 and C12 are oriented quite differently. This is indicated by the N1−C8−C7−S1 and N1−C12−C13−S2 torsion angles, which are 46.4(4)° and −121.3(3)°, respectively. The locations of the S atoms clearly indicate that the conformation observed for **L5** in the solid state is not suitable for tridentate NS_2 coordination to a metal ion.

In [$RuCl_2$(**L5**)(PPh_3)]·$2CCl_4$, the metal assumes a distorted octahedral coordination sphere and the ligand **L5** coordinates

(22) Canovese, L.; Chessa, G.; Marangoni, G.; Pitteri, B.; Uguagliati, P.; Visentin, F. *Inorg. Chim. Acta* **1991**, *186*, 79.
(23) Köseoglu, F.; Kiliç, E.; Uysal, D. *Talanta* **1995**, *42*, 1875.
(24) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

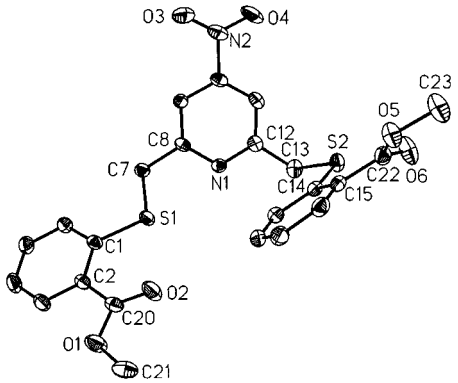


Figure 2. Perspective ORTEP[20] view of the ligand **L5** showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

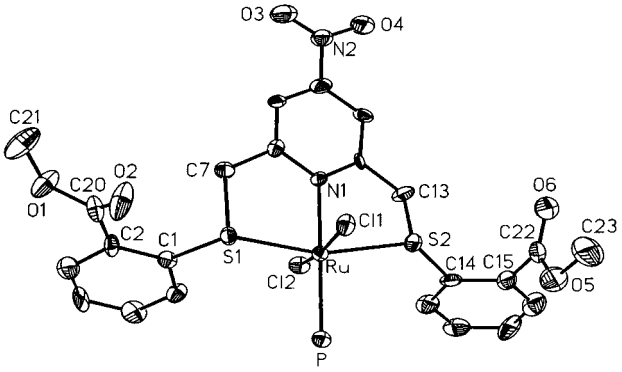


Figure 3. Simplified ORTEP[20] drawing of the complex unit in $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$ showing 30% displacement ellipsoids. Phenyl groups of PPh_3 ligand and hydrogen atoms are omitted for clarity.

tridentately via the two S atoms and the N atom of the pyridine ring to Ru(II). The three remaining coordination positions of Ru(II) are occupied by two chloride ions and the P atom of PPh_3. The distortion of the coordination sphere is clearly indicated by variation of the bond angles (Table 2), and nonplanarity of the atom group Ru, S1, S2, and N1 of the coordination sphere. The atoms Ru, S1, P, and N1 are approximately in the same plane, and S2 deviates from the plane by 0.646(9) Å. Also the orientations of the S atoms with respect to the pyridine ring are different: the S1 atom is in the same plane as the pyridine ring, but S2 deviates from (is above) the plane by 0.812(18) Å.

In the monomeric Ru(II) complexes of 2,6-bis(phenylthiomethyl)pyridine derivatives,[16] reported recently, the derivatives exhibit versatile conformations, and different from that in $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$, even coordination modes of the pyridine derivatives are similar in all of the complexes. Thus the observed geometrical arrangement of the **L5** ligand in $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$ is a further example of the versatility of the NS_2 coordinating ligands. In the compared complexes,[16] the pyridine rings are rotated with respect to the two "substituent arms" so that C7 and C13 are on the opposite sides of the NS_2-Ru plane. This is a noticeable difference compared with $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$. However, all of these complexes show a common phenomenon. In the case when PPh_3 ligand is coordinated to the metal, the bulky substituent is pushing the neighboring ligands, and thus the position of the PPh_3 ligand seems to determine the orientations of the Ph groups or Ph derivatives connected to the S atoms.

Conclusions

The NS_2(*S*-aryl) ligands reported here are all derivatives of 2,6-bis(phenylthiomethyl)pyridine. Its coordinating sites are the nitrogen at the pyridine moiety and the two thioethers bonded to the phenyl rings. The question was whether substituents on the pyridine moiety would alter more substantially the properties of the parent ligand than substituents on the phenyl rings. To achieve these results difficult and time-consuming syntheses of ligands with substituents on pyridine have been carried out. Evidence has demonstrated, however, that by adequately choosing the substituents on phenyl similar results can be obtained. In spite of this possibility, it is clear that the pK_A in NS_2(*S*-aryl) ligands is more dependent on the incorporation of electron-withdrawing groups on the pyridine than on the phenyl, but that the pK_A lowering with respect to 2,6-bis(phenylthiomethyl)-pyridine is very different from the case between pyridine and 3-chloropyridine where the pK_A of the last is 2.41 units lower.[25] Electron-withdrawing substituents on the rings produce a shift to higher $E_{1/2}$ both on Cu(II)/Cu(I) and on Ru(III)/Ru(II) couples. Again, the shift is larger for substitution on the pyridine than on the *S*-phenyl ring but, as mentioned, appropriate substituents shall produce equivalent results.

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Supporting Information Available: Details of the X-ray structure determinations, in CIF format, of the structures of **L5** and $[RuCl_2(\mathbf{L5})(PPh_3)]\cdot 2CCl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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