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Synthesis and characterization of ruthenium(II) complexes incorporating 4′-phenyl-terpyridine and triphenylphosphine

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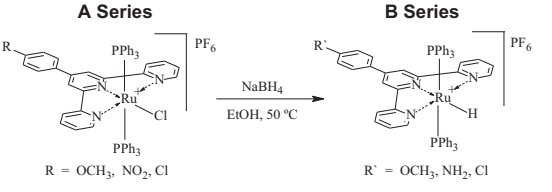

The syntheses of two new series of ruthenium(II) complexes incorporating substituted 4′-phenyl-terpyridine, triphenylphosphine, and chloride (A Series) or hydride (B Series) are reported. In both series 4′-phenyl-terpyridine incorporated substituents of varying electronic character at the 4-position: 4′-(4-chlorophenyl)-2,2′ : 6′,2″-terpyridine (ClPh-tpy); 4′-(4-nitrophenyl)-2,2′ : 6′,2″-terpyridine (NO_2Ph-tpy) and 4′-(4-methoxyphenyl)-2,2′ : 6′,2″-terpyridine (OMePh-tpy). The complexes have been characterized by elemental analysis and UV–vis, IR, and NMR spectroscopy and their electrochemical properties studied. The substituents on the 4′-phenyl-terpyridine ligand influence the properties of the metal center. For all complexes prepared, λ_{max} of a characteristic low energy band in the UV–vis spectrum was found to move to shorter wavelengths as the solvent polarity increased (a hypsochromic shift). For the B series complexes, the low energy band was broader and undergoes a small shift to lower frequencies as a result of the substitution of chloride by a hydride. The ^{1}H and ^{31}P NMR spectra clearly indicate that the geometry of the 4′-phenyl-terpyridine ligand is meridional in the complexes, with the two triphenylphosphines *trans* to each other. Upon optimization of the experimental procedures the yields increased to 70% for the B series complexes.

Keywords: Ruthenium complexes; Polypyridine complexes; Terpyridine complexes

1. Introduction

Polypyridine complexes of ruthenium(II) have attracted interest due to their tunable photophysical and electrochemical properties combined with high thermal and chemical robustness [1]. They are used as light harvesters in dye-sensitized solar cells [2–4], luminescent emitters in light-emitting electrochemical cells [5–7], potential anticancer and imaging agents in

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phototherapy [8–10], sensors for ions [11–16] and small molecules [17, 18], photocatalysts for water splitting [19, 20], hydrogen production [21–24], CO_2 reduction [21, 23, 25], and many other chemical reactions [23, 26–29], components in mixed valence systems [30–35], light upconversion systems, [36–39] and molecular memory devices [40–42].

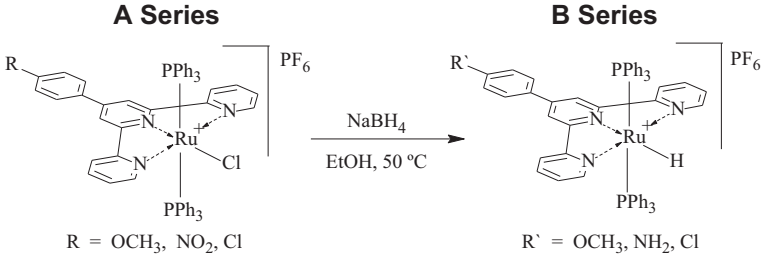
Numerous complexes have been synthesized in the search for new catalysts for hydroformylation, hydrogenation, or carbonylation of olefins. For these systems the preferred transition metals are those from the second and third transition series, ruthenium, rhodium, palladium, and platinum [43–48]. Ruthenium complexes used as catalysts have adequate charge density [44], and several strategies for their synthesis have been proposed. Thus, ruthenium complexes with nitrogen and phosphorus [45] containing electron-donating atoms in their structures can be used to modulate the charge density on the metal. This can be carried out using groups with different electronic character on a polypyridine ligand structure [46], or using phosphorous ligands in which some substituents have been modified. Properties can be studied using UV–vis spectroscopy and cyclic voltammetry [47]. Such studies may help rationalize their catalytic activity [48].

This work describes the synthesis of two new series of ruthenium(II) complexes, $[Ru(L_1)(PPh_3)_2X]PF_6$, where L_1 is substituted 4′-phenyl-terpyridine and X = Cl (A Series) or hydride (B Series). In both series the 4′-phenyl-terpyridine ligand is substituted at the 4-position with substituents of varying electronic character, RPh-tpy (R = Cl, OMe, NO_2), as shown in scheme 1.

2. Experimental

2.1. *Instrumentation and measurements*

FT-IR spectra were obtained using a Bruker IFS-66 V spectrophotometer (KBr cell, 0.2 mm length) between 4000 and 400 cm^{-1}. ^1H NMR spectra were recorded on a 350 MHz Bruker spectrometer. Absorption spectra were measured on a Specord S100 (Analytikjena) spectrophotometer using acetonitrile and methylene chloride as solvents. Electrochemical data were acquired with a cyclic voltammeter using an Autolab/PGSTAT30 Potentiostat/Galvanostat with Autolab 4.9 software. Working solutions of the complexes were prepared in anhydrous acetonitrile which was dried by refluxing over CaH_2 under N_2 for 2 h and distilled prior to use. Tetrabutylammonium perchlorate (TBAP, 0.1 M) was used as a supporting electrolyte. Measurements were made with a three-electrode configuration cell. The working electrode was vitreous carbon and the reference and counter electrodes were



Scheme 1.

Ag/AgCl and platinum wire, respectively. Potentials are reported as $E_{1/2}$ values determined from $E_{1/2} = ½ (E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

2.2. *Materials and preparations*

All chemicals were reagent-grade and used as received unless otherwise specified. 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 2-acetylpyridine, sodium hydroxide, ammonium acetate, sodium borohydride, ruthenium trichloride trihydrate, ammonium hexafluorophosphate, chloroform, acetonitrile, ethanol, methanol, methylene chloride, diethylether, chloroform-d, acetonitrile-d_3, and acetone-d_6 were purchased from Aldrich. The ligands 4′-(4-chlorophenyl)-2,2′ : 6′,2″-terpyridine (ClPh-tpy), 4′-(4-nitrophenyl)-2,2′ : 6′,2″-terpyridine (NO_2Ph-tpy), and 4′-(4-methoxyphenyl)-2,2′ : 6′,2″-terpyridine (OMePh-tpy) were prepared according to literature procedures [49]. [Ru(ClPh-tpy)Cl_3] and [Ru(NO_2Ph-tpy)Cl_3] were prepared by procedures analogous to those previously used for their [Ru(tpy)Cl_3] analogues [50], whereas [$RuCl_2(PPh_3)_3$] was synthesized following literature procedures [51]. The complexes were purified by column chromatography with activated aluminum oxide, Brockman I, standard grade, 150 mesh, from Aldrich.

2.3. *Synthesis*

2.3.1. [Ru(ClPh-tpy)$(PPh_3)_2$Cl]PF_6. [$RuCl_2(PPh_3)_3$] (0.40 g, 0.417 mmol) and ClPh-tpy (0.143 g, 0.417 mmol) dissolved in methanol (20 mL) were placed in a round bottom flask (50 mL) and the mixture was refluxed for 6 h. Upon cooling to room temperature, NH_4PF_6 (0.100 g, 0.612 mmol) was added and the system was refluxed for 2 h under stirring. The resulting brown-orange solution was concentrated and a solid precipitated after adding diethyl ether. The solid was purified by column chromatography over activated aluminum oxide using a toluene/acetone mixture (1 : 1) as eluent. The combined eluates were evaporated to dryness by rotary evaporation, the residual solid dissolved in a minimal amount of acetone, and diethyl ether added to induce crystallization. The solution stood overnight in a freezer, yielding a microcrystalline brown-orange solid. Yield: 86% (0.413 g), m.p. 310 °C (d). IR (KBr, ν cm^{-1}): 3058(C–H), 1612(C=C), 1480(C=N), 1186(P-Ph), 1088(P-Ph), 841 (PF_6^-), 557(PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 9.30(d, H_d, ^3J $H_{d\text{-}c}$ = 8.23), 8.22(d, H_a, ^3J H_{a-b} = 5.73), 8.07(s, H_e), 7.95(AB, H_f, ^3J H_{f-g} = 8.59), 7.88(t, H_c, ^3J H_{c-d} = 8.23), 7.68 (AB, H_g, ^3J $H_{g\text{-}f}$ = 8.59), 7.44(td, H_b, ^3J H_{b-a} = 5.73), 7.34–7.15(m, PPh_3). ^{31}P NMR (δ ppm): 17.1 (s, PPh_3), −146(qt, PF_6). Anal. Calcd (%) for $C_{57}H_{44}Cl_2F_6N_3P_3Ru$: C, 59.54; H, 3.86; N, 3.65. Found (%): C, 58.59; H, 3.83; N, 3.80.

2.3.2. [Ru(OMePh-tpy)$(PPh_3)_2$Cl]PF_6. The ligand OMePh-tpy (0.220 g, 0.648 mmol) and [$RuCl_2(PPh_3)_3$] (0.621 g, 0.648 mmol) in methanol (40 mL) were placed in a round bottom flask (50 mL) and the mixture refluxed for 5 h. Upon cooling the solution to room temperature, NH_4PF_6 (0.150 g, 0.920 mmol) was added and the system is stirred for 2 h. The precipitate was filtered and purified by chromatography over aluminum oxide using a toluene/acetone mixture (1 : 1) as eluent. The eluate was evaporated to dryness by rotary evaporation, the residue dissolved in a minimal amount of acetone and diethyl ether added to precipitate the solid, which was filtered and dried in a vacuum oven at 60 °C. Yield:

95% (0.702 g), m.p. 300 °C (d). IR (KBr, ν cm^{-1}): 3057(C–H), 1604(C=C), 1518(C=N), 1179(P-Ph), 1091(P-Ph), 845(PF_6^-), 557(PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 9.29 (d, H_d, ^3J $H_{d\text{-}c}$ = 7.16), 8.21(d, H_a, ^3J H_{a-b} = 6.09), 8.01(s, H_e), 7.87 (AB, H_f, and d, H_c, ^3J $H_{f\text{-}c}$ = 8.95), 7.40 (dd, H_b, ^3J H_{b-a} = 6.09), 7.34–7.17(AB, H_g and PPh_3), 3.96 (s, OCH_3). ^{31}P NMR (δ ppm): 17.1 (s, PPh_3), −146 (qt, PF_6^-). Anal. Calcd (%) for $C_{58}H_{47}ClF_6N_3OP_3Ru$: C, 60.00; H, 4.14; N, 3.67. Found (%): C, 60.00; H, 4.20; N, 3.80.

2.3.3. [Ru(NO_2Ph-tpy)(PPh_3)$_2$Cl]PF_6. [$RuCl_2(PPh_3)_3$] (0.500 g, 0.520 mmol) and NO_2Ph-tpy (0.180 g, 0.520 mmol) in ethanol (50 mL) were placed in a round bottom flask (100 mL) and the mixture refluxed for 6 h. Upon cooling to room temperature, NH_4PF_6 (0.150 g, 0.920 mmol) was added and the solution stirred at room temperature for 2 h. The resulting solid was separated by filtration and purified by chromatography over aluminum oxide using a toluene/acetone mixture (1 : 1) as eluent. The eluate was evaporated to dryness in a rotary evaporator, the residue was dissolved in a minimum amount of acetone and diethyl ether was added to precipitate the product. The solid was filtered and dried in a vacuum oven at 60 °C. Yield: 92% (0.56 g), m.p. 180 °C (d). IR (KBr, ν cm^{-1}): 3053(C–H), 1599(C=C), 1516(C=N), 1480(NO_2), 1346(NO_2), 1183(P-Ph), 1088(P-Ph), 841(PF_6^-), 557 (PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 9.33(d, H_d, ^3J $H_{d\text{-}c}$ = 7.31), 8.24(d, H_a, ^3J H_{a-b} = 4.87), 8.20(s, H_e), 8.48(AB, H_f, ^3J H_{f-g} = 9.74), 8.22(AB, H_g, ^3J $H_{g\text{-}f}$ = 9.74), 7.91(t, H_c, ^3J H_{c-d} = 7.31), 7.46(t, H_b, ^3J H_{b-a} = 4.87), 7.35–7.16 (m, PPh_3). ^{31}P NMR (δ ppm): 17.1 (s, PPh_3), −146 (qt, PF_6^-). Anal. Calcd for $C_{57}H_{44}ClN_4O_2P_3Ru$ (%): C, 56.90; H, 3.82; N, 4.83. Found (%): C, 56.95; H, 3.89; N, 5.45.

2.3.4. [Ru(ClPh-tpy)(PPh_3)$_2$H]PF_6. [RuCl(ClPh-tpy)(PPh_3)]PF_6 (0.250 g, 0.218 mmol) dissolved in ethanol (30 mL) and $NaBH_4$ (0.200 g, 2.64 mmol) were placed in a round bottom flask (50 mL). The mixture was stirred under nitrogen and heated at 50 °C for 3 h. After this time, NH_4PF_6 (0.050 g, 0.306 mmol) was added and the system refluxed for 2 h. Upon cooling, acetone was added (30 mL), the precipitate was filtered by gravity, and purified by chromatography over aluminum oxide using a toluene/acetone mixture (1 : 1) as eluent. The combined eluates were evaporated to dryness by rotary evaporation and the residue dissolved in minimal amount of acetone. Diethyl ether was added and the mixture was allowed to stand overnight in a freezer. The obtained microcrystalline solid was filtered through a fritted Büchner funnel, recrystallized from diethyl ether and dried in a vacuum oven at 60 °C. Yield: 58% (0.112 g), m.p. 180 °C (d). IR (KBr, ν cm^{-1}): 3051(C–H), 1960 (Ru-H), 1608(C=C), 1479(C=N), 1179(P-Ph), 1092(P-Ph), 697, 840(PF_6^-), 557(PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 8.50(s, H_e), 8.29(d, H_d, ^3J $H_{d\text{-}c}$ = 7.31), 8.08(AB, H_f, ^3J H_{f-g} = 8.52), 8.02(d, H_a, ^3J H_{a-b} = 7.31), 7.76(AB, H_g and H_c), 7.27(m, PPh_3), 6.83(dd, H_b, ^3J H_{b-a} = 6.09), −5.7(t, H_h, ^3J Ph_3-H = 24). ^{31}P NMR (δ ppm): 49.9 (s, PPh_3), −146(m, PF_6^-). Anal. Calcd (%) for $C_{57}H_{45}ClF_6N_3P_3Ru$: C, 61.38; H, 4.07; N, 3.77. Found (%): C, 60.31; H, 3.89; N, 3.81.

2.3.5. [Ru(OMePh-tpy)(PPh_3)$_2$H]PF_6. [RuCl(OMePh-tpy)(PPh_3)]PF_6 (0.250 g, 0.218 mmol) dissolved in ethanol (30 mL) and $NaBH_4$ (0.350 g, 9.25 mmol) were placed in a round bottom flask (50 mL). The mixture was stirred under nitrogen and heated at 60 °C for 3 h. After this time, NH_4PF_6 (0.050 g, 0.306 mmol) was added and the system was refluxed for 2 h. Upon cooling, acetone was added (30 mL) and the mixture was filtered by gravity. The

solution was concentrated and then purified by chromatography over aluminum oxide using a toluene/acetone mixture (1 : 1) as eluent. The combined eluates were evaporated to dryness by rotary evaporation. The residue was dissolved in a minimal amount of acetone, diethyl ether added and the resulting mixture was allowed to stand overnight in a freezer. The obtained microcrystalline solid was filtered through a fritted Büchner funnel, recrystallized from acetone and diethyl ether, and dried in an oven at 60 °C under vacuum. Yield: 77% (0.186 g), m.p. 180 °C (d). IR (KBr, ν cm^{-1}): 3052(C–H), 1967(Ru-H), 1604(C=C), 1517(C=N), 1182(P-Ph), 1091(P-Ph), 696, 840(PF_6^-), 557(PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 8.44(s, H_e), 8.27 (d, H_d, ^3J H_{d-c} = 8.22), 7.98(AB, H_f and d, H_a), 7.66(t, H_c, ^3J H_{c-d} = 8.22) 7.25(PPh_3 and AB, H_g), 6.81(t, H_b, ^3J H_{b-a} = 5.48), 3.97(s, OCH_3), −6.02(t, H_h, ^3J Ph_3-H = 24). ^{31}P NMR (δ ppm): 49.9(s, PPh_3), −146(m, PF_6^-). Anal. Calcd (%) for $C_{58}H_{48}F_6N_3OP_3Ru$: C, 62.7; H, 4.35; N, 3.78. Found (%): C, 61.18; H, 4.20; N, 3.62.

2.3.6. [Ru(NH_2Ph-tpy)(PPh_3)$_2$H]PF_6. [RuCl(NO_2Ph-tpy)(PPh_3)]PF_6 (0.260 g, 0.227 mmol) was dissolved in ethanol (50 mL) in a round bottom flask (100 mL) and $NaBH_4$ (0.340 g, 8.987 mmol) added. The mixture was stirred under nitrogen and heated at 55 °C for 6 h. Upon cooling to room temperature, the mixture was filtered by gravity and the solution concentrated. Upon adding diethyl ether a solid was obtained which was separated by filtration and purified by chromatography over neutral alumina using a toluene/acetone mixture (1 : 1) as eluent. The combined eluates were evaporated to dryness in a rotary evaporator, the residue was dissolved in a minimum amount of acetone, diethyl ether added, and the mixture was allowed to stand overnight in a freezer. The obtained microcrystalline solid was filtered through a fritted Büchner funnel, recrystallized from ethyl ether and dried in an oven at 60 °C under vacuum. Yield: 59% (0.150 g), m.p. 289 °C (d). IR (KBr, ν cm^{-1}): 3388(NH_2), 3048(C–H), 1967(Ru-H), 1597(C=C), 1522(C=N), 1298(NH_2), 1185(P-Ph), 1090(P-Ph), 696, 838(PF_6^-), 557(PF_6^-). ^{1}H NMR (δ ppm; J, Hz): 8.38(s, H_e), 8.24(d, H_d, ^3J H_{d-c} = 8.52), 7.93(d, H_a, ^3J H_{a-b} = 6.09), 7.79(AB, H_f, ^3J H_{f-g} = 8.52), 7.63(t, H_c, ^3J H_{c-d} = 8.52), 7.63(t, H_b, ^3J H_{b-a} = 8.52), 7.26(m, PPh_3), 6.92(AB, H_g, ^3J H_{g-f} = 8.52), 5.2 (s, br, NH_2), −5.8(t, H_h, ^3J Ph_3-H = 24). ^{31}P NMR (δ ppm): 49.8 (s, PPh_3), −146(m, PF_6^-). Anal. Calcd (%) for $C_{57}H_{47}F_6N_4P_3Ru$: C, 62.46; H, 4.32; N, 5.11. Found (%): C, 62.01; H, 4.24; N, 5.16.

3. Results and discussion

3.1. *Synthesis*

The ligands used in the ruthenium complexes were prepared according to a literature procedure [49]. Complexes of Series A were synthesized by the direct reaction of $RuCl_2(PPh_3)_3$ with R-tpy with a reasonable yield (R = Cl, OMePh-tpy and NO_2Ph-tpy with 95, 92 and 58% yield, respectively). The hydride complexes (Series B) were synthesized from the corresponding A series complexes and an excess of $NaBH_4$ in ethanol (10 : 1) at 50 °C, resulting in the substitution of the chloride by hydride [52] (scheme 1). This differs from the procedure reported in the literature for related analogs with terpyridine substituted by tert-butyl groups [53]. The intermediate complexes were initially obtained as Cl^- salts and subsequently precipitated as PF_6^- salts. The latter complexes were used in the synthesis of the hydride complexes. All A and B series complexes are stable in air.

3.2. *Infrared spectroscopy*

Infrared spectra of the complexes show the characteristic bands of PF_6^- at 840 and 560 cm^{-1}. The typical stretches of the pyridine ring appear at 1600 and 1518 cm^{-1}. For both the A and B series, absorptions for triphenylphosphine are at 1170–1185 cm^{-1} and 1090 cm^{-1} for the P-Ph bond. For $[Ru(NO_2Ph\text{-}tpy)(PPh_3)_2Cl]PF_6$, two additional absorptions due to asymmetric and symmetric stretching in the $–NO_2$ group are at 1480 and 1346 cm^{-1}. These absorptions disappear after reaction with $NaBH_4$, in which case the product is $[Ru(NH_2Ph\text{-}tpy)(PPh_3)_2H]PF_6$, characterized by absorptions of $–NH_2$ at 3500 and 3388 cm^{-1} due to the asymmetric and symmetric N–H bond stretches, the 1600 cm^{-1} band due to bending of NH_2 and the 1298 cm^{-1} band due to stretching of the phenyl-nitrogen bond. While the substitution reaction occurs, reduction of the nitro group in the terpyridine also takes place [54].

3.3. *UV–visible spectroscopy*

UV–vis spectra for the A series were recorded in acetonitrile. Bands were observed in the UV region with high molar extinction coefficients which are assigned to terpyridine and triphenylphosphine centered (LC) $\pi \rightarrow \pi^*$ transitions (figure 1). These intraligand transitions are at lower energies compared to those of $[Ru(tpy)_2](PF_6)_2$, which may be due to increased electronic delocalization of the conjugated ligand which stabilizes the LUMO (π^*) orbital. The spectral data are given in table 1. The complexes present a broad low energy band of moderate intensity with $\varepsilon \sim 3000$ and 7000 M^{-1} cm^{-1} centered at 490–500 nm and a shoulder at 450 nm, which can be attributed to metal-to-ligand charge transfer (MLCT), Ru(II)$\rightarrow\pi^*$ (L) [55], and correspond to typical transitions observed for ruthenium (II) complexes incorporating tridentate polypyridine ligands such as tpy [56, 57] and tppz [58]. Further support for this low energy band assignment was obtained by recording spectra using solvents with varying polarities. A shift toward higher energy was observed as the polarity of the solvent increased; that is, a hypsochromic shift to shorter wavelengths. The spectral position and intensity of these low energy transitions are similar to those observed for other polypyridine complexes [59]. The λ_{max} value observed for these electronic transitions is dependent on the electronic nature of the pendant moiety at the 4′ position of the central ring of terpyridine; that is, the value increases according to the sequence $–OCH_3 < –Cl < NO_2$ (480, 485, 491 nm, respectively, measured in acetonitrile).

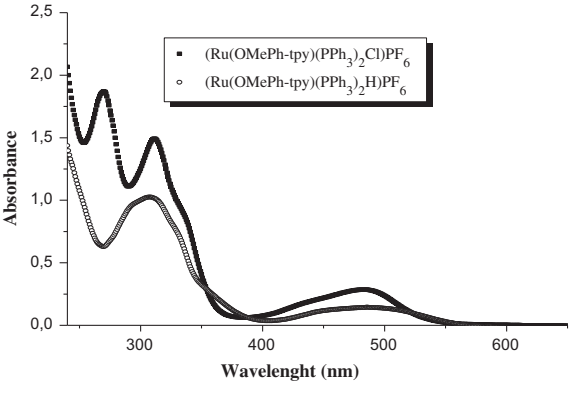


Figure 1. UV–vis spectra of the Ru complexes in CH_3CN solutions.

Table 1. Spectroscopical data for the ruthenium series A and series B complexes.

Complexes	λ_{abs}/(nm) ε($\times 10^{-3}$, M^{-1} cm^{-1})					
	$\pi \rightarrow \pi^*$				MLCT	
$[Ru(tpy)(PPh_3)_2Cl]PF_6$[a]	268(43.2)	312(23.2)	330sh		431sh	473 (3,62)
$[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$	269 (37.3)	312 (30.3)			434 (4.3)	480 (5.6)
$[Ru(OMePh\text{-}tpy)(PPh_3)_2H]PF_6$	230 (37.8)	307 (32.3)				487 (5.6)
$[Ru(NO_2Ph\text{-}tpy)(PPh_3)_2Cl]PF_6$	269 (26.2)	308 (24.9)	339 (13.4)	372 (5.7)	435 (4.5)	491 (7.7)
$[Ru(NH_2Ph\text{-}tpy)(PPh_3)_2H]PF_6$		311 (25.8)	345 (22.5)			489 (7.7)
$[Ru(ClPh\text{-}tpy)(PPh_3)_2Cl]PF_6$	268 (31.0)	313 (26.3)			430 (3.1)	485 (6.3)
$[Ru(ClPh\text{-}tpy)(PPh_3)_2H]PF_6$	285 (27.3)	315 (22.1)				487 (5.0)

[a]Ref. [8].

For complexes of the B series the low energy band appears broader and undergoes a small shift to lower frequencies, which is probably attributable to substitution of a chloride by a hydride (figure 1). Intense bands at 300 nm correspond to intraligand transitions [59, 60].

3.4. *Electrochemistry*

Cyclic voltammetry was used to study the electrochemical properties of the complexes in acetonitrile using TBAP as the supporting electrolyte. Values of $E_{1/2}$ for Ru(II)/Ru(III) couples are compiled in table 2. Complexes of the A Series, $[Ru(RPh\text{-}tpy)(PPh_3)_2Cl]PF_6$, show quasi-reversible potentials at +0.821, +0.947 and +0.932 for OMe, Cl, and NO_2, respectively. These differences correlate with the electronic character of the phenyl-R substituents over the 4′-position of the central ring of the terpyridine and are comparable to the redox potential of $[Ru(tpy)(PPh_3)_2Cl]PF_6$ [50, 54].

The reduction potentials of the substituted terpyridine ligand in the type A complexes are quasi reversible or irreversible [see figure 2(a)] for $[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$]. However, reversible and quasi-reversible couples are observed in the complexes incorporating hydride [the separation of anodic and cationic peaks is between 65 and 45 mV, depending on the terpyridine substituent, see figure 2(b) for $[Ru(OMePh\text{-}tpy)(PPh_3)_2H]PF_6$]. The oxidation potentials of the metal in complexes with the same terpyridine, but with chloride or hydride coordinated to the metal center, show a shift to negative values for complexes

Table 2. Electrochemical data for ruthenium series A and series B complexes.

Complexes	$E_{1/2}$Ox (Volt) (ΔE (mV))	$E_{1/2}$Red (Volt) (ΔE (mV))			Ref.
$[Ru(tpy)(PPh_3)_2Cl][PF_6]$	+0.89 (70)				[8, 11]
$[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$	+0.821 (60)	−1.3088 pa	−1.30 pc, −1.73 pc,	−1.547 pc, −1.856 pc	This work
$[Ru(ClPh\text{-}tpy)(PPh_3)_2Cl]PF_6$	+0.947 (61)	−1.170 pc	−1.411 pc		This work
$[Ru(NO_2Ph\text{-}tpy)(PPh_3)_2Cl]PF_6$	+0.932 (49)	−1.347 pa	−1.502pc		This work
$[Ru(NH_2Ph\text{-}tpy)(PPh_3)_2H]PF_6$	+0.577 pa +1.589 (44) +1.839 pa	−1.539 (65)	−1.918 pc		
$[Ru(OMePh\text{-}tpy)(PPh_3)_2H]PF_6$	+0.567 +1.633 (170) +1.936 pa	−1.578 (51)	−1.866 pc,	−1.966 pc	This work
$[Ru(ClPh\text{-}tpy)(PPh_3)_2H]PF_6$	+0.583 pa +1.585 (49) +1.824 pa	−1.541 (46)	−1.907 pc		This work

containing hydrides, which indicates that the metal can be oxidized more easily. Thus for $[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$ and $[Ru(OMePh\text{-}tpy)(PPh_3)_2H]PF_6$, the oxidation potentials are +0.821 and +0.567 V, respectively. The same can be observed for $[Ru(ClPh\text{-}tpy)(PPh_3)_2Cl]PF_6$, $[Ru(ClPh\text{-}tpy)(PPh_3)_2H]PF_6$ and $[Ru(NH_2Ph\text{-}tpy)(PPh_3)_2H]PF_6$ (oxidation potentials, +0.821 and +0.567, +0.557 V, respectively).

3.5. *NMR spectroscopy*

^1H NMR spectral data for the complexes are given in section 2.3 of the Experimental section. $[Ru(ClPh\text{-}tpy)(PPh_3)_2Cl]PF_6$ (A Series) exhibits signals at 9.30(d, H_d), 8.23(d, H_a), 8.07(s, H_e), 7.95(system AB, H_f), 7.88(t, H_c), 7.68(system AB, H_g), 7.44(td, H_b), and 7.34–7.15(m, PPh_3) associated with the coordinated tpy. A singlet at 3.96 ppm reveals the presence of $-OCH_3$ in $[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$. The aromatic protons of PPh_3 are two broad multiplets. Analogous trends were observed for the ^1H NMR spectra of [Ru

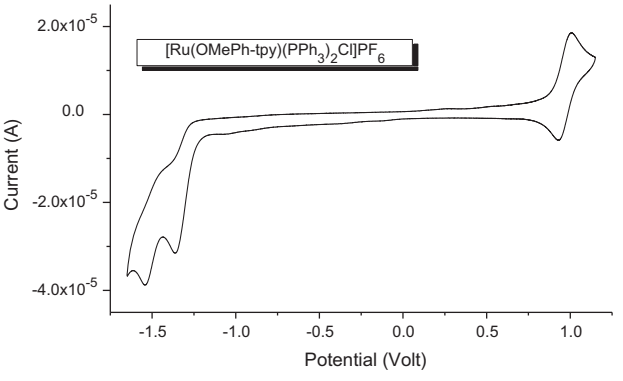


Figure 2(a). Cyclic voltammetry of $[Ru(OMePh\text{-}tpy)(PPh_3)_2Cl]PF_6$.

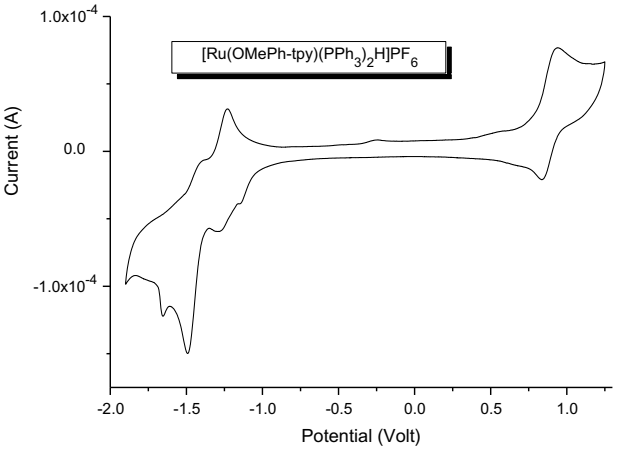


Figure 2(b). Cyclic voltammetry of $[Ru(OMePh\text{-}tpy)(PPh_3)_2H]PF_6$.

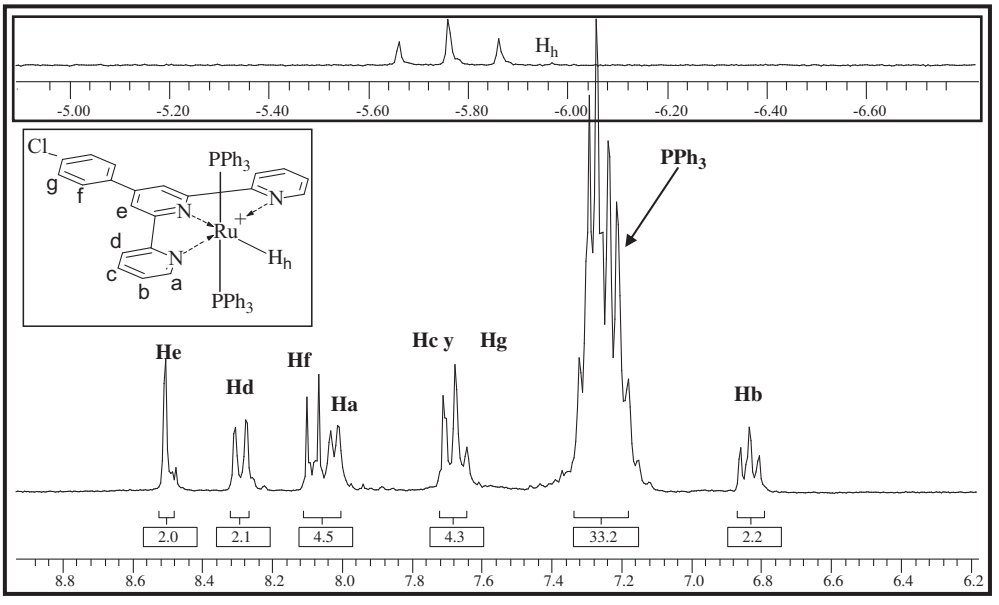


Figure 3. ^{1}H NMR spectrum for [Ru(ClPh-tpy)$(PPh_3)_2$H]PF_6.

(OMePh-tpy)$(PPh_3)_2$Cl]PF_6 and [Ru$(NO_2$Ph-tpy)$(PPh_3)_2$Cl]PF_6, except that H_g from the AB system overlapped with aromatic protons of PPh_3 for [Ru(OMePh-tpy)$(PPh_3)_2$Cl]PF_6. The ^{1}H NMR spectrum of the B series [Ru(ClPh-tpy)$(PPh_3)_2$H]PF_6 exhibited signals at 8.50(s, H_e), 8.28(d, H_d), 8.08(system AB, H_f) 8.02(d, H_a), 7.76 (AB system, H_g), 7.27(m, PPh_3), and 6.83(t, H_b). An additional high field triplet for the hydride is at −5.7(t, H_h), consistent with coupling of the two phosphorus with the hydride.

The combined ^{1}H and ^{31}P NMR spectra allowed formulation of the structures of the complexes. Figure 3 shows the proton assignments for a B series complex which are similar to the corresponding A series complex, with the hydride proton signal observed at −5.8 ppm. The signal of the hydride ligand appears as a triplet with a 24 Hz coupling constant. Protons of the terpyridine and triphenylphosphine were also assigned. A phosphorus singlet at 52 ppm (triphenylphosphine) and a multiplet (PF_6^- anion) were also observed in the ^{31}P NMR spectrum.

4. Conclusion

Two series of ruthenium complexes incorporating choride (A Series) or hydride (B Series) have been prepared and characterized. The optimization of the experimental procedures increases the yield of the hydride complexes to 70%. The ^{1}H and ^{31}P NMR spectra clearly indicate that terpyridine in each complex is located in a meridional coordination geometry, whereas the triphenylphosphines are *trans* to each other. The terpyridine ligand substituents affect the properties of the metal center, which leads to an increase in the oxidation potentials and to a decrease in the energy for the MLCT band.

Disclosure statement

No potential conflict of interest was reported by the authors.

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