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Paramagnetic Ru(III) complexes of tridentate ligands: Characterization of useful intermediates for heteroleptic Ru(II) complexes

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ABSTRACT

Paramagnetic $Cl_3Ru(L)$ complexes of tridentate ligands (**2a**: L = **1a** = 4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine; **2b**: L = **1b** = 6-(*p*-bromophenyl)-2,4-dipyrid-2-yl-1,3,5-triazine) were synthesized in a high-yield method with facile isolation of these useful synthons. The complexes were isolated in high purity and were characterized by several methods, including standard techniques such as ^{1}H NMR and electrospray ionization mass spectrometry. The ^{1}H NMR of the complexes displayed peaks from +10 to −37 ppm, with the protons *ortho* to the nitrogen atoms coordinated to the paramagnetic centre being shifted the most (**2a**: $H_{6,6''} = -35.3$ ppm; **2b**: $H_{6,6''} = -26.1$ ppm), while the protons on the non-bonding phenyl rings were relatively unchanged with respect to their uncomplexed ligands. The electronic absorption spectra of the complexes displayed both ^{1}LMCT bands (Cl-to-Ru, **2a**: λmax = 405 nm; **2b**: λmax = 420 nm) and ^{1}MLCT (Ru-to-L, **2a**: λmax = 486 nm; **2b**: λmax = 567 nm) bands. Due to the ease of purification and high yields, the use of complex **3**, first introduced by Chatt, is the method of choice to form $Cl_3Ru(L)$ complexes of tridentate ligands.

Ruthenium polypyridyl complexes are attractive species as chromophores in light-harvesting asssemblies which aim to convert solar energy into chemical energy [1–5]. They display desirable electrochemical and photophysical properties such as : (i) a strong absorption in the visible region of the spectrum; (ii) a relatively long lifetime of the emissive ^{3}MLCT (Metal-to-Ligand Charge-Transfer) excited-state at room temperature (r.t.); (iii) a capacity for energy and electron transfer; (iv) and in some cases, a capacity for reversible multi-electron storage [6]. The prototypical $Ru(bpy)_3^{2+}$ unit (bpy = 2,2′-bipyridine) has a long-lived r.t. excited state [7], however, the stereogenic $Ru(bpy)_3^{2+}$ motif leads to complicated mixtures of isomers in larger supramolecular assemblies [8–10]. In contrast, the achiral $Ru(tpy)_2^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) motif gives unique products in polymetallic complexes when substituted symmetrically on the tpy rings [10,11], thus simplifying the synthesis of oligomeric species. The synthetic pathway commonly followed to obtain heteroleptic Ru(II)-polypyridine complexes is *via* intermediate derivatives of Ru(III), $LRuCl_3$ (with L = neutral tridentate polypyridine ligand) [11–15]. In a subsequent step, this intermediate is traditionally refluxed in a polar solvent with silver salts and 1 equiv. of L′ (where L′ = different neutral tridentate polypyridine ligand), to give a heteroleptic complex $[LRuL']^{2+}$. Although, this protocol is widely used, characterization of the Ru(III) intermediates remains limited due to the paramagnetic nature of Ru(III)-polypyridine complexes produced in this way, even though it has been demonstrated that coordination complexes of Ru(III) can be studied by ^{1}H NMR [16], an essential tool in synthetic chemistry. Another important technique is ESI-MS (Electro-Spray Ionization Mass Spectrometry), commonly used in identification of coordination complexes, and even, in the elucidation of reaction mechanisms [17]. The main difficulty with poorly soluble neutral species lies in the successful ionization of the compound and its identification, which is sometimes obscured by fragmentation processes arising from the ionization process. We report herein the characterization by ^{1}H NMR and ESI-MS of neutral paramagnetic Ru(III) intermediates, **2a–b**, using a Ru(III) precursor initially described by Chatt et al. over thirty years ago [18].

Complex **3** presents significant advantages when the syntheses of tridentate ligands are multi-step or are only available in low yields [19]. In particular, **3** is: (i) more soluble than $RuCl_3 \cdot xH_2O$, allowing a variety of solvents to be used for synthesis; and (ii) successfully complexed by tridentate ligands in refluxing CH_3CN, due to the easy displacement of thioether ligands avoiding the need for polar and reducing solvents (such as alcohols and DMF). Meyer et al. [20]. previously reported the synthesis of $(tpy)RuCl_3$ as being more convenient and high-yielding starting from $RuCl_3 \cdot xH_2O$ than from **3**. However, even in the case of ligands **1a–b**, we found out that **3** leads

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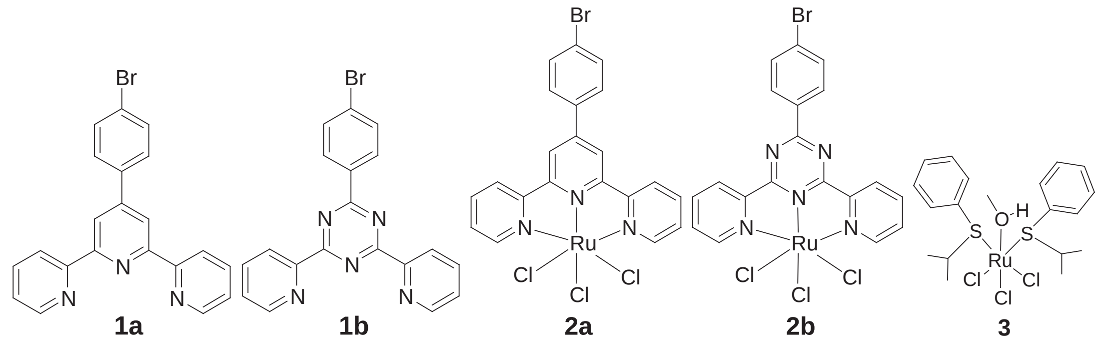
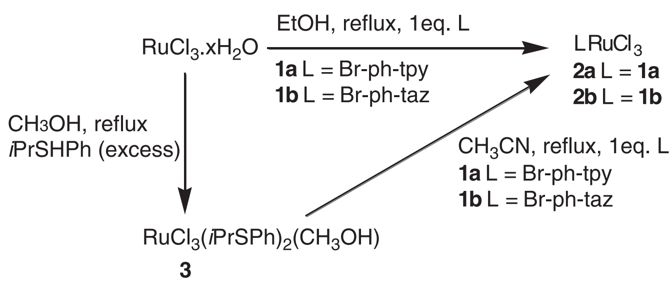


Chart 1. Chart. Structures for ligands **1a–b**, complexes **2a–b** and precursor **3**.



Scheme 1. Synthesis of $LRuCl_3$ (**2a–b**) from $RuCl_3 \cdot xH_2O$ (classical way) *vs.* from $RuCl_3(iPrSPh)_2(CH_3OH)$ (**3**).

to easier purification of the desired complexes **2a–b**. Indeed, removal of the cationic homoleptic Ru(II) complex which forms in the synthesis of is of crucial importance when one aims at further complexation, in a 'step-by-step' approach toward supramolecular asssemblies [21] (Chart 1, Scheme 1 and Table 1).

Ligands **1a** [22] and **1b** [23] were synthesized following published procedures. Precursor **3** was synthetized following the initial report from Chatt et al. [18],. and was fully characterized by ^1H NMR, ESI-MS, elemental analysis, UV–visible absorption and X-ray diffraction (see Supplementary Information). The high-resolution ESI-MS analysis allowed identification of **3** and some fragmentation pathways : [**3**-2Cl–$CH_3OH + e^-$]$^+$; [**3**-2Ph]$^+$ and [**3**-Ph-*i*Pr]$^+$. The X-ray structure confirmed the formation of the *mer* isomer (Fig. 1), predicted by Chatt, and required for complexation to a tridentate polypyridine-type ligand.

The presence of the paramagnetic centre Ru(III) significatively influences the chemical shifts of the protons from the organic moiety (Fig. 2). Signals observed between 9.8 and 7.3 ppm correspond to a diamagnetic decomposition by-product, forming in a few hours in DMSO by slow reduction of Ru(III)[16c] (over the duration of data acquisition). Signals corresponding to the paramagnetic species (major product) were observed between 10 and −37 ppm (Fig. 2).

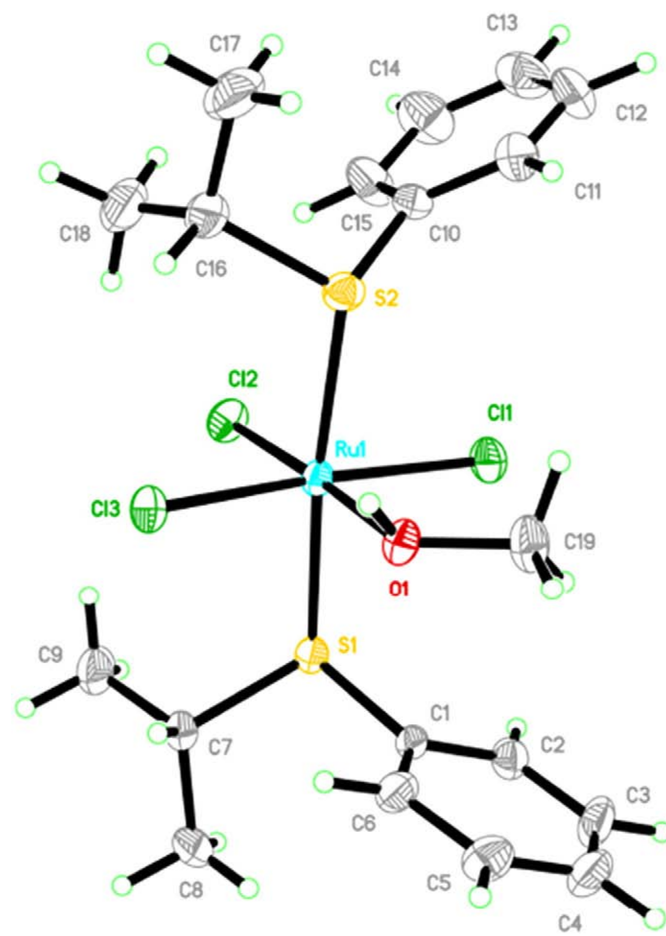


Fig. 1. ORTEP diagram of **3** (thermal ellipsoides drawn at 50% probability), confirming the *mer* geometry, needed to accommodate a coordinating tridentate ligand.[2]

Table 1
Absorption data, measured in acetonitrile, for complexes **2a–b** and **3**.

Compound	λ/nm (ε/M^{-1} cm^{-1})				
2a	227 (21145)	285 (19950) LC π–π* **1a**	306 (14900) LC π–π* **1a**	405 (6010) LMCT Cl→Ru	486 (2950) MLCT Ru→**1a**
2b	–	294 (24600) LC π–π* **1b**	320 (sh) LC π–π* **1b**	420 (7480) LMCT Cl→Ru	567 (2700) MLCT Ru→**1b**
3	253 (15440) LC π–π* Sulfide	–	–	404 (4570) LMCT Cl→Ru	479 (1110) MLCT Ru→sulfide

The unpaired electron of Ru(III) accelerates the relaxation processes of neighboring nuclei, masking the coupling interaction ^1H–^1H with a distance-dependancy of $1/r^3$. Thus, all signals appear as broad singlets, except for the most distant protons $H_{2''}$ and $H_{3''}$, belonging to the phenyl ring (*vide infra*). Assignment of the different signals remains an important step in the understanding of these species : (a) giving access to information on electronic effects, in the molecule itself and by comparision within a family of derivatives; (b) allowing NMR ^1H monitoring of complexation reactions (particularly important whenever Thin-Layer Chromatography is not a viable option). At first, the observed loss of signals multiplicity prevented a meaningful assignment

2 CIF information is available as CCDC 774603.

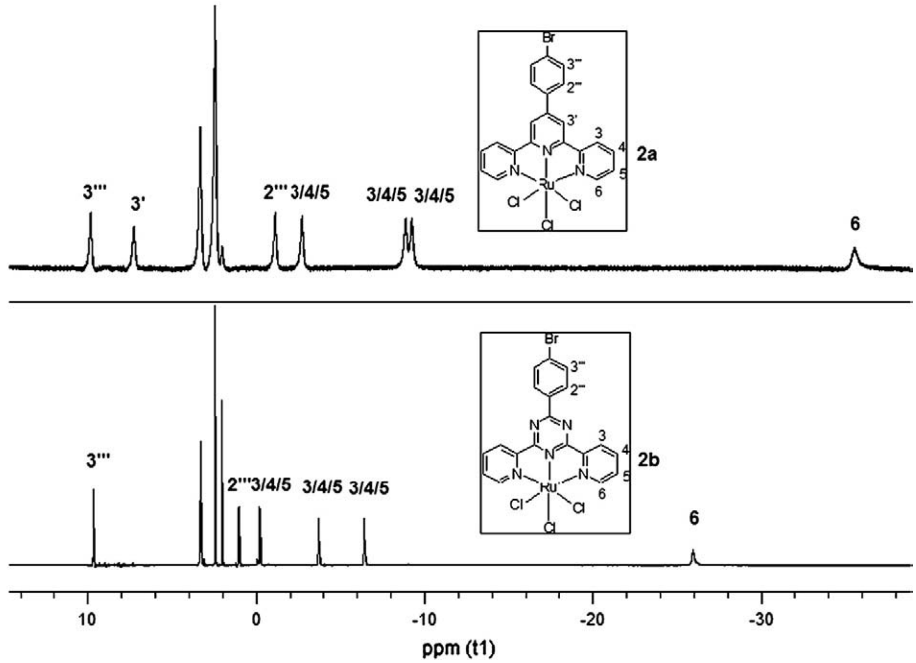


Fig. 2. ^1H NMR spectra for **2a** and **2b**, recorded at r.t. (400 MHz, DMSO-d_6): the upfield shift of the protons from the ligand, due to the Ru(III) centre, is not the same in **2b** compared to **2a**, the protons being further influenced by the electron-deficient effect of the triazine.

of the peaks, except for the peaks at 9.86 ppm and −1.02 ppm. These two peaks were the only ones to display multiplicity (doublets), due to their remoteness with respect with the paramagnetic centre, and they were assigned to the protons of the phenyl ring (this assignment was further confirmed by COSY ^1H–^1H, showing coupling between these two protons). HMQC ^1H–^{13}C and TOCSY (Total Correlation Spectroscopy) experiments on model complex **2a** led to the majority of peaks being assigned. However, the signals at −2.67, −8.76 and −9.17 ppm were not assigned as the proton at −35.3 ppm did not couple with its neighboring proton(s) even with longer acquisition times. Finally, ^1H NMR (d_6-DMSO, 700 MHz, 298 K) gave the following assignment: δ 9.85 (d, J = 16 Hz, 2H, $H_{3''}$), 7.28 (br, 2H, $H_{3'}$), −1.04 (d, J = 17 Hz, 2H, $H_{2''}$), −2.67 (br, 2H, $H_{3/4/5}$), −8.76 (br, 2H, $H_{3/4/5}$), −9.17 (br, 2H, $H_{3/4/5}$), and −35.3 (br, 2H, H_6) ppm. In **2b**, the electron deficiency of the triazine motif has a contrary effect on the chemical shifts of the protons from the pyridyl rings. Unexpectedly, in **2a**, the shielding effect of the paramagnetic centre is more important on the $H_{2''}$ protons than on the $H_{3'}$ protons, suggesting that the angular dependancy of the paramagnetic effect has to be taken into account.

Compounds **2a–b** have an absorption profile common to ruthenium polypyridyl complexes, albeit with bands at higher energy than usually observed, due to the effect of the chloro ligands (Fig. 3). The intense absorption bands in the UV region of the spectrum are due to π–π* transitions Ligand-Centered (LC), whereas the bands in the visible region are due to ^{1}MLCT transitions. Two main low-lying transitions are expected for each compound: a ^{1}MLCT Ru → **1a–b** and a ^{1}LMCT Cl → Ru, with the latter at higher energy than the former.

In conclusion, the characteristic ^1H NMR signals for intermediate Ru(III) complexes make them useful tools to verify the purity of these important precursors for heteroleptic Ru(II) complexes. Precursor **3** turned out to be generally more useful for complexation of tridentate ligands than $RuCl_3 \cdot xH_2O$, leading to easier purification of reaction mixtures, and of particular use when the tridentate ligands are only afforded in multiple steps and in low yields.

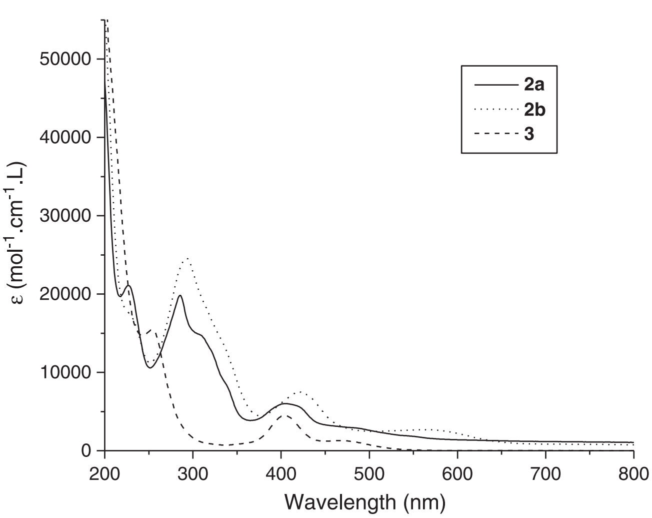


Fig. 3. Electronic absorption spectra of **2a** (solid line), **2b** (dotted line) and **3** (dashed line) in acetonitrile.

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Appendix A. Supplementary data[3]

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.12.011.

[3] See Supplementary Information for synthetic descriptions and characterization.

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