

# Thermally and Photochemically Induced Co-ordination Changes in Ruthenium(II) Bis(2,2'-bipyridine) Complexes containing Pyridyltriazole Ligands†

Barbara E. Buchanan,<sup>a</sup> Peter Degn,<sup>a</sup> Juan Martin Pavon Velasco,<sup>a</sup> Helen Hughes,<sup>a</sup> Bernadette S. Creaven,<sup>a</sup> Conor Long,<sup>a</sup> Johannes G. Vos,<sup>\*,a</sup> R. Alan Howie,<sup>b</sup> Ronald Hage,<sup>c</sup> John H. van Diemen,<sup>c</sup> Jaap G. Haasnoot<sup>c</sup> and Jan Reedijk<sup>c</sup>

<sup>a</sup> School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

<sup>b</sup> Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, UK

<sup>c</sup> Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA, Leiden, The Netherlands

A series of Ru<sup>II</sup>(bipy)<sub>2</sub> complexes (bipy = 2,2'-bipyridine) containing monodentate co-ordinated pyridyltriazole ligands has been prepared and characterised. The species are obtained by either thermal or photochemical methods. The co-ordination mode of the products obtained has been investigated using spectroscopic techniques. The molecular structure of one of the products, bis(2,2'-bipyridine)chloro-[3-methyl-1-(pyridin-2-yl)-1,2,4-triazole]ruthenium(II) hexafluorophosphate, has been determined. The compound crystallises in the triclinic space group *P* $\bar{1}$  with unit-cell parameters *a* = 8.599(12), *b* = 13.503(16), *c* = 16.526(16) Å,  $\alpha$  = 89.88(9),  $\beta$  = 117.22(8),  $\gamma$  = 111.08(10)° and *Z* = 2. The pyridyltriazole is co-ordinated *via* the N<sup>4</sup> nitrogen atom. In the compounds containing monodentate 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole the ligand is most likely co-ordinated *via* the N<sup>1</sup> atom. The conversion of the photoproduct acetonitrilebis(2,2'-bipyridine)[4-methyl-3-(pyridin-2-yl)-1,2,4-triazole]ruthenium(II) into the parent complex containing the chelating pyridyltriazole ligand by thermal as well as photochemical methods is reported.

At present much attention is being paid to the study of ruthenium(II) diimine type complexes because of their possible application in solar energy conversion and in electrocatalytic systems. Detailed investigations have been carried out to understand the physical properties of such compounds, and<sup>1-3</sup> in particular their photochemical and photophysical properties. One of the problems in the application to solar energy systems is the small but significant photodecomposition of compounds such as [Ru(bipy)<sub>3</sub>]<sup>2+</sup> (bipy = 2,2'-bipyridine).<sup>3-6</sup> It has been proposed that the photochemically initiated labilisation of the chelating bipy ligands takes place through an intermediate in which the ligand is bound in a monodentate fashion.<sup>7</sup> However, no direct structural evidence for the presence of such a co-ordination mode has so far been published.

We have recently started a systematic investigation of the physical properties of a series of Ru<sup>II</sup>(bipy)<sub>2</sub> compounds containing pyridyltriazoles and related ligands. The aim of these studies is to fine tune the photophysical properties of these compounds and also to study the interactions between metal centres in compounds with such types of ligands as bridging ligands.<sup>8</sup> Because of the asymmetry of these ligands (see Fig. 1), it was also decided to investigate the possibility of monodentate co-ordination. It was hoped that more information about the nature of the monodentate intermediates proposed above could be obtained.

In this contribution we report the synthesis and characterisation of a series of compounds of the type [Ru(bipy)<sub>2</sub>(L-L')X]<sup>n+</sup>, where L-L' is a monodentate co-ordinated pyridyltriazole ligand, X = Cl<sup>-</sup> or MeCN and *n* = 1 or 2, respectively. The ligands investigated are shown in Fig. 1. The compounds have been prepared by thermal or photochemical means and the co-

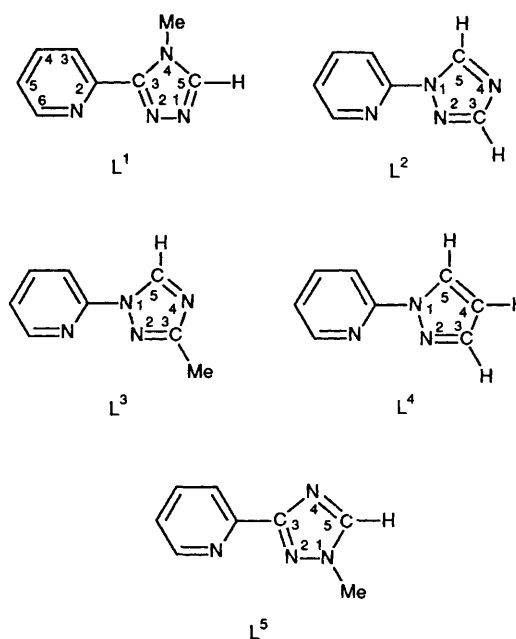


Fig. 1 Structure of the ligands: 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L<sup>1</sup>); 1-(pyridin-2-yl)-1,2,4-triazole (L<sup>2</sup>); 3-methyl-1-(pyridin-2-yl)-1,2,4-triazole (L<sup>3</sup>); 1-(pyridin-2-yl)pyrazole (L<sup>4</sup>); and 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L<sup>5</sup>)

ordination mode of the monodentate ligands investigated with spectroscopic and electrochemical techniques. The crystal and molecular structure of one of the products obtained thermally, [Ru(bipy)<sub>2</sub>(L<sup>3</sup>)Cl]PF<sub>6</sub>, is also reported. Part of the work

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

reported has been presented recently as a preliminary communication.<sup>9</sup>

## Experimental

**Instrumental Procedures.**—The UV/VIS spectra were obtained using a Shimadzu UV 240 instrument. Emission spectra were obtained on a Perkin-Elmer LS-5 luminescence spectrometer equipped with a red-sensitive Hamamatsu R 928 photomultiplier tube; the data obtained were not corrected for photomultiplier response. Proton NMR spectra were recorded on a Bruker WM-300 MHz spectrometer; peak positions are measured relative to SiMe<sub>4</sub>. Electrochemical measurements were carried out using an EG&G Par model 174A polarographic analyser with an EG&G 175 Universal Programmer. A saturated potassium calomel electrode (SCE) was used as reference electrode. Measurements were carried out in AnalaR grade MeCN dried over molecular sieves, with 0.1 mol dm<sup>-3</sup> NEt<sub>4</sub>ClO<sub>4</sub> as a supporting electrolyte using glassy carbon electrodes. The scan rate was 100 mV s<sup>-1</sup>. High-performance liquid chromatography (HPLC) experiments were carried out using methods reported in earlier papers.<sup>8h,i</sup> Small-scale photochemical experiments using 1 cm pathlength cells were carried out using a 400 W medium-pressure mercury lamp with a glass cut-off filter. Preparative photochemical experiments were carried out using a medium-pressure 400 W lamp fitted in an immersion well, again fitted with a glass filter. Elemental analyses were carried out at University College Dublin.

**X-Ray Crystallography of [Ru(bipy)<sub>2</sub>(L<sup>3</sup>)Cl]PF<sub>6</sub>.**—A black crystal of dimensions 0.35 × 0.35 × 0.35 mm was used. Its density was determined using the flotation method and dibromomethane-hexane mixtures.

**Crystal data.** C<sub>28</sub>H<sub>24</sub>ClF<sub>6</sub>N<sub>8</sub>PRu, *M* = 753.75, triclinic, space group *P* $\bar{1}$ , *a* = 8.599(12), *b* = 13.503(16), *c* = 16.526(16) Å,  $\alpha$  = 89.88(9),  $\beta$  = 117.22(8),  $\gamma$  = 111.08(10)°, *U* = 1561(4) Å<sup>3</sup>, *D<sub>m</sub>* = 1.66 Mg m<sup>-3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.60 Mg m<sup>-3</sup>, *F*(000) = 756,  $\mu$ (Mo-K $\alpha$ ) = 6.55 cm<sup>-1</sup>,  $\lambda$ (Mo-K $\alpha$ ) = 0.710 69 Å.

**Data collection and processing.** A Nicolet P3 four-circle diffractometer was used for the data collection. The unit-cell parameters were refined by least-squares procedures and 4272 reflections were recorded at room temperature (with 2 $\theta$  in the range 0–60°). The intensities of two reference reflections were measured at intervals of 50 reflections throughout the data collection and showed no significant variation. The intensities were converted into structure amplitudes in the usual way. The ranges of *h*, *k* and *l* used were 0–11, –17 to 17 and –21 to 21.

**Structure solution and refinement.** The structure was solved by conventional Patterson and Fourier methods and refined to a final *R* value of 0.069 (*R'* = 0.076) by full-matrix least squares using SHELX 76 and SHELXS 86 programs.<sup>10</sup> First isotropic and then anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms were placed at their calculated positions. The function minimised was  $w(|F_o| - |F_c|)^2$ , where  $w = 0.8057(\sigma^2 F + 0.01 F^2)$ . The discrepancy indices are defined as  $R = \Sigma|\Delta F|/\Sigma|F_o|$  and  $R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$ . Scattering factors and anomalous-dispersion corrections were taken from ref. 11.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

**Materials.**—The compounds [Ru(bipy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O<sup>12</sup> and L<sup>1</sup>, L<sup>2</sup>, L<sup>4</sup> and L<sup>5</sup> (ref. 8a) were prepared as reported in the literature. All other reactants were reagent-grade materials and were used as received.

**Synthesis of 3-Methyl-1-(pyridin-2-yl)-1,2,4-triazole (L<sup>3</sup>).**—This ligand was prepared by the method reported for L<sup>2</sup>,<sup>8a</sup> using 3-methyl-1,2,4-triazole, m.p. 86–87 °C. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO]:  $\delta$

8.89 (1 H, s, H<sup>5</sup>), 8.29 (1 H, d, H<sup>6</sup>), 7.83 (1 H, d, H<sup>3</sup>), 7.67 (1 H, t, H<sup>4</sup>), 7.21 (1 H, q, H<sup>5</sup>) and 2.21 (3 H, s, CH<sub>3</sub>).

**Synthesis of the Ruthenium Complexes.**—The complexes [Ru(bipy)<sub>2</sub>(L<sup>1</sup>)]PF<sub>6</sub><sub>2</sub> **1** and [Ru(bipy)<sub>2</sub>(L<sup>2</sup>)]PF<sub>6</sub><sub>2</sub> **2** were prepared as reported before.<sup>8a</sup>

[Ru(bipy)<sub>2</sub>(L<sup>2</sup>)]PF<sub>6</sub><sub>2</sub>: <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: pyridyltriazole ligand,  $\delta$  10.19 (1 H, s, H<sup>5</sup>), 8.57 (1 H, d, H<sup>3</sup>), 8.35 (1 H, s, H<sup>3</sup>), 8.31 (1 H, t, H<sup>4</sup>), 7.62 (1 H, d, H<sup>6</sup>) and 7.48 (1 H, t, H<sup>5</sup>); bipyridine ligands, 8.86–8.77 (4 H, m, H<sup>3</sup>), 8.24–8.10 (4 H, m, H<sup>4</sup>), 8.08 (1 H, d, H<sup>6</sup>), 7.90 (1 H, d, H<sup>6</sup>), 7.71 (2 H, t, H<sup>6</sup>) and 7.60–7.50 (4 H, m, H<sup>5</sup>).

[Ru(bipy)<sub>2</sub>(L<sup>3</sup>)]PF<sub>6</sub><sub>2</sub> **3**. This compound was prepared as reported for **2**. Yield 750 mg (87%) (Found: C, 39.0; H, 2.8; N, 13.2. C<sub>28</sub>H<sub>24</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub>Ru requires C, 38.9; H, 2.8; N, 13.0%). <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: pyridyltriazole ligand,  $\delta$  10.05 (1 H, s, H<sup>5</sup>), 8.62 (1 H, d, H<sup>3</sup>), 8.31 (1 H, t, H<sup>4</sup>), 7.79 (1 H, d, H<sup>6</sup>), 7.51 (1 H, q, H<sup>5</sup>) and 1.81 (3 H, s, CH<sub>3</sub>); bipyridine ligands, 8.89–8.85 (4 H, m, H<sup>3</sup>), 8.38–8.20 (4 H, m, H<sup>4</sup>), 8.36 (1 H, d, H<sup>6</sup>), 8.11 (1 H, s, H<sup>6</sup>), 8.07 (1 H, d, H<sup>6</sup>) 7.91 (1 H, s, H<sup>6</sup>) and 7.66–7.57 (4 H, m, H<sup>5</sup>).

[Ru(bipy)<sub>2</sub>(L<sup>1</sup>)Cl]PF<sub>6</sub>·H<sub>2</sub>O **4**. **Method A.** The complex [Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (520 mg, 1 mmol) was heated at reflux in acetone-ethanol (50:50, 150 cm<sup>3</sup>). The ligand L<sup>1</sup> (190 mg, 1.2 mmol) was dissolved in acetone (5 cm<sup>3</sup>) and added to the reaction mixture over a period of 10 min. The mixture was heated for 30 min. The solvent was removed by rotary evaporation, the residue dissolved in methanol-diethyl ether (3:1) and purified by column chromatography using neutral alumina and methanol-diethyl ether (3:1) containing 1% acetone as eluent. A dark red fraction, later found to be the monodentate species, eluted first and the solvent was removed by rotary evaporation. The residue was dissolved in water (5 cm<sup>3</sup>) and precipitated by addition to aqueous NH<sub>4</sub>PF<sub>6</sub>. Yield 527 mg (80%) (Found: C, 43.3; H, 3.2; Cl, 4.4; N, 14.1. C<sub>28</sub>H<sub>26</sub>ClF<sub>6</sub>N<sub>8</sub>OPRu requires C, 43.5; H, 3.4; Cl, 4.6; N, 14.8%). <sup>1</sup>H NMR (CD<sub>3</sub>CN): pyridyltriazole ligand,  $\delta$  9.00 (1 H, s, H<sup>5</sup>) 8.80 (d, 1 H, H<sup>6</sup>), 8.00 (1 H, d, H<sup>4</sup>), 7.70 (1 H, d, H<sup>3</sup>), 7.55 (1 H, m, H<sup>5</sup>) and 3.98 (3 H, s, CH<sub>3</sub>); bipyridine ligands, 9.95 (1 H, d, H<sup>6</sup>), 8.60 (1 H, d, H<sup>6</sup>), 8.45 (1 H, d, H<sup>3</sup>), 8.33 (2 H, d, H<sup>3</sup>), 8.21 (1 H, d, H<sup>3</sup>), 8.03 (2 H, m, H<sup>4</sup>), 7.88 (1 H, d, H<sup>6</sup>), 7.75 (3 H, m, 2H<sup>4</sup>, H<sup>6</sup>), 7.50 (1 H, m, H<sup>5</sup>), 7.40 (1 H, m, H<sup>5</sup>) and 7.15 (2 H, m, H<sup>5</sup>).

**Method B.** This compound was also obtained in a small amount by photochemical means. Complex **1** (100 mg) was irradiated in MeCN–0.01 mol dm<sup>-3</sup> LiCl (300 cm<sup>3</sup>) in an immersion well at room temperature. The solution was continuously purged with nitrogen. The reaction progress was followed by HPLC. The irradiation time was typically 20 min. After completion of the reaction the solvent was evaporated *in vacuo* at room temperature and the monodentate intermediate was separated using semi-preparative HPLC. The small amounts of material obtained were unstable in the HPLC mobile phase. By freezing out the aqueous component a small amount of complex was obtained. This material proved to be NMR pure but contained a substantial amount of KNO<sub>3</sub>, originally present in the mobile phase. Elemental analysis was therefore not satisfactory. Attempts to purify the compound further failed, but the proton NMR spectrum obtained was identical to that of compound **4** as prepared by method A.

[Ru(bipy)<sub>2</sub>(L<sup>2</sup>)Cl]PF<sub>6</sub> **5**. The complex [Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (520 mg, 1 mmol) was heated under reflux in ethanol-acetone (70:30, 150 cm<sup>3</sup>). Small aliquots of L<sup>2</sup> (175 mg, 1.2 mmol) dissolved in ethanol were added over a period of 10 min. The mixture was refluxed for 20 min. The solvent was removed on the rotary evaporator and the residue dissolved in a small amount of methanol-diethyl ether (3:1). Purification employed column chromatography on neutral alumina with methanol-diethyl ether (3:1) as eluent. The dark red fraction of the monodentate species was eluted first; the orange fraction of the bidentate species was removed with methanol. Fraction 1 was precipitated by addition to aqueous NH<sub>4</sub>PF<sub>6</sub>, filtered off and dried *in vacuo*. Yield 396 mg (52%) (Found: C, 43.8; H, 3.0; Cl,

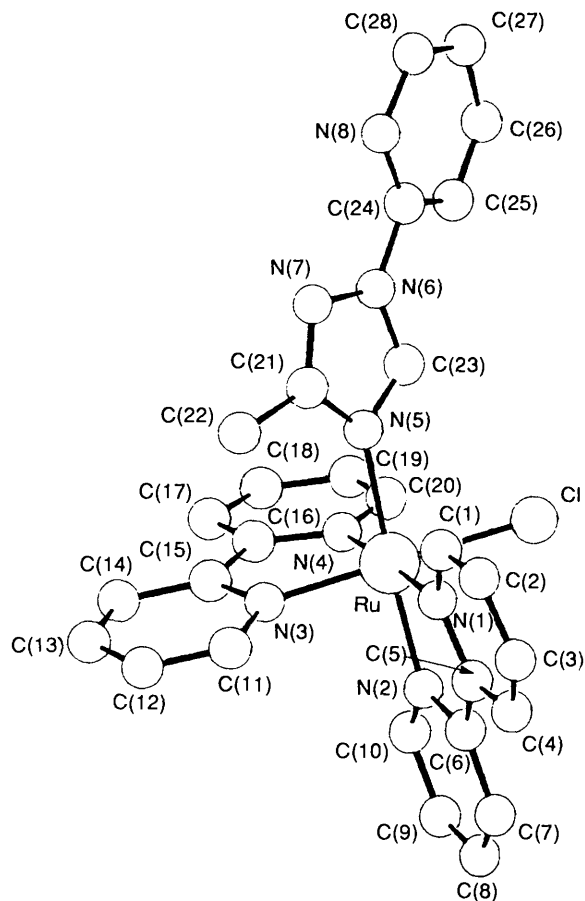


Fig. 2 A SCHAKAL drawing<sup>14</sup> of the  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]^+$  cation with the atom numbering

4.7; N, 14.6.  $\text{C}_{27}\text{H}_{22}\text{ClF}_6\text{N}_8\text{PRu}$  requires C, 43.8; H, 3.0; Cl, 4.8; N, 15.1%.  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ : pyridyltriazole ligand,  $\delta$  9.62 (1 H, s,  $\text{H}^5$ ), 8.49 (1 H, d,  $\text{H}^6$ ), 8.08 (1 H, t,  $\text{H}^4$ ), 8.02 (1 H, s,  $\text{H}^3$ ), 7.80 (1 H, t,  $\text{H}^3$ ) and 7.50 (1 H, q,  $\text{H}^5$ ); bipyridine ligands, 10.08 (1 H, d,  $\text{H}^6$ ), 8.86 (1 H, d,  $\text{H}^6$ ), 8.72–8.52 (4 H, m,  $\text{H}^3$ ), 8.20–7.85 (7 H, m,  $4\text{H}^4$ ,  $2\text{H}^6$ ,  $\text{H}^5$ ), 7.66 (1 H, t,  $\text{H}^5$ ), 7.38 (1 H, t,  $\text{H}^5$ ) and 7.28 (1 H, t,  $\text{H}^5$ ).

$[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]\text{PF}_6$  6. This compound was prepared as for 5. Yield 347 mg (46%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): pyridyltriazole ligand,  $\delta$  10.27 (1 H, s,  $\text{H}^5$ ), 8.53 (1 H, d,  $\text{H}^6$ ), 8.08 (1 H, t,  $\text{H}^4$ ), 7.82 (1 H, d,  $\text{H}^3$ ), 7.50 (1 H, q,  $\text{H}^5$ ) and 1.67 (3 H, s,  $\text{CH}_3$ ); bipyridine ligands, 10.11 (1 H, d,  $\text{H}^6$ ), 8.90 (1 H, d,  $\text{H}^6$ ), 8.73 (1 H, d,  $\text{H}^3$ ), 8.65 (1 H, d,  $\text{H}^3$ ), 8.60 (2 H, d,  $\text{H}^3$ ), 8.21 (1 H, d,  $\text{H}^6$ ), 8.18 (2 H, m,  $\text{H}^4$ ), 8.00–7.60 (5 H, m,  $2\text{H}^5$ ,  $\text{H}^6$ ,  $2\text{H}^4$ ), 7.34 (1 H, t,  $\text{H}^5$ ) and 7.28 (1 H, t,  $\text{H}^5$ ).

$[\text{Ru}(\text{bipy})_2(\text{L}^1)(\text{MeCN})][\text{PF}_6]_2$  7. Complex 1 (30 mg) was irradiated in MeCN (300  $\text{cm}^3$ ) in an immersion well at room temperature. The solution was continuously purged with nitrogen. The reaction progress was followed by HPLC. The irradiation time was typically 6 min. After completion of the reaction the solvent was evaporated *in vacuo* at room temperature and the monodentate intermediate was separated using semi-preparative HPLC. The product was then precipitated using aqueous  $\text{NH}_4\text{PF}_6$  (0.5 g in 10  $\text{cm}^3$ ). Overall yield after HPLC separation 60%. Recrystallisation did not improve the purity of the sample, as a small amount of the starting material was always formed (about 2–5%). No elemental analysis was therefore carried out.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): pyridyltriazole ligand,  $\delta$  9.24 (1 H, s,  $\text{H}^5$ ), 8.69 (1 H, d,  $\text{H}^6$ ), 7.90 (1 H, t,  $\text{H}^4$ ), 7.80 (1 H, d,  $\text{H}^3$ ), 7.50 (1 H, t,  $\text{H}^5$ ), 4.12 (3 H, s,  $\text{CH}_3$ ) and 2.55 (3 H, s,  $\text{CH}_3\text{CN}$ ); bipyridine ligands, 9.67 (1 H, d,  $\text{H}^6$ ), 9.10 (1 H, d,  $\text{H}^6$ ), 8.82 (1 H, d,  $\text{H}^3$ ), 8.70 (2 H, q,  $\text{H}^3$ ), 8.58 (1 H, d,  $\text{H}^3$ ), 8.36 (1 H, t,  $\text{H}^4$ ), 8.26 (1 H, t,  $\text{H}^4$ ),

8.10–7.80 (5 H, m,  $2\text{H}^4$ ,  $2\text{H}^5$ ,  $\text{H}^6$ ) 7.79 (1 H, d,  $\text{H}^6$ ) and 7.45 (2 H, m,  $\text{H}^5$ ).

## Results and Discussion

**General.**—In many papers dealing with the photochemistry of metal diimine complexes, compounds containing monodentate co-ordinated ligands have been proposed as intermediates in the photolabilitation of these complexes.<sup>7</sup> Our aim was to prepare such intermediates. The two approaches taken are based on thermal and photochemical methods in conjunction with the use of HPLC. The thermal reaction is based on the well documented difference in the lability of the two chloride atoms in  $[\text{Ru}(\text{bipy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ . Replacement of the first chloride is facile and occurs in organic solvents at low temperatures, such as acetone and ethanol. Replacement of the second chloride is however much more difficult and requires either higher-boiling solvents or the addition of water.<sup>13</sup> All thermal reactions were therefore carried out in acetone or ethanol in the absence of water. In this manner a series of compounds with the overall formula  $[\text{Ru}(\text{bipy})_2(\text{L}-\text{L}')\text{Cl}]\text{PF}_6$  was obtained for the ligands  $\text{L}^1$ – $\text{L}^3$ . Elemental analysis, spectroscopic and structural data suggest that the pyridyltriazole ligand is bound in a monodentate fashion (see below). For  $\text{L}^4$  and  $\text{L}^5$  no such products were obtained and only bidentate co-ordination was observed for these ligands.

Attempts to isolate photochemically produced complexes containing monodentate co-ordinated pyridyltriazole ligands were based on the observation that when compounds of the type  $[\text{Ru}(\text{bipy})_2(\text{L}-\text{L}')][\text{PF}_6]_2$  are irradiated in MeCN UV/VIS spectra taken during the photolysis do not show isobestic points. The HPLC analyses of such reactions show clearly the formation of an intermediate during the photolysis of compounds 1–3. The intermediate was most clearly observed during the photolysis of 1. To identify the nature of this species a preparative photolysis of compound 1 was carried out (see Experimental section), in which the intermediate, 7, was isolated in good yield. The material obtained was about 95% pure; during recrystallisation a small part of the initially pure compound was converted back into the starting material. As the yield of the intermediate was less in the photolysis of 2 and 3 no attempt was made to isolate these species, but the similarities in peak shape, retention time and absorption spectrum very strongly suggest that the intermediates formed during the photolysis of 1–3 have a similar structure.

From the photolysis of complex 1 in MeCN–0.01 mol  $\text{dm}^{-3}$  LiCl another intermediate was isolated also containing the triazole ligand co-ordinated in a monodentate fashion but this time with a chloride, rather than a MeCN, as the sixth ligand.

**Crystal Structure of  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]\text{PF}_6$ .**—Fractional coordinates are given in Table 1, relevant bond distances and angles in Table 2. A SCHAKAL drawing of the  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]^+$  cation is shown in Fig. 2, together with the atom labelling system used.

Fig. 2 shows clearly that  $\text{L}^3$  is co-ordinated in a monodentate fashion and also substantiates the presence of a chloride atom. The co-ordination geometry around the central metal ion is slightly distorted octahedral with  $\text{L}^3$  co-ordinated through the  $\text{N}^4$  nitrogen [ $\text{N}(5)$ ]. It is important to note here that the  $\text{N}^4$  atom in the triazole ring is a non-chelating co-ordination site and that the structure of this compound is not the one expected for a possible photochemically produced intermediate. For the latter, co-ordination through one of the chelating sites, the pyridine nitrogen or  $\text{N}^2$  of the triazole ring, would be more reasonable. As expected from the starting material used, the bipy ligands are in a *cis* configuration. The average Ru–N distance for the bipy ligands of 2.035 Å is within the range normally found for such compounds.<sup>15–18</sup> The distance between the central metal ion and  $\text{N}(5)$  is substantially longer at 2.131(6) Å, possibly related to steric factors. Both bidentate

**Table 1** Fractional atomic coordinates for non-hydrogen atoms ( $\times 10^4$ ) for  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]\text{PF}_6$ , with estimated standard deviations (e.s.d.s) in parentheses

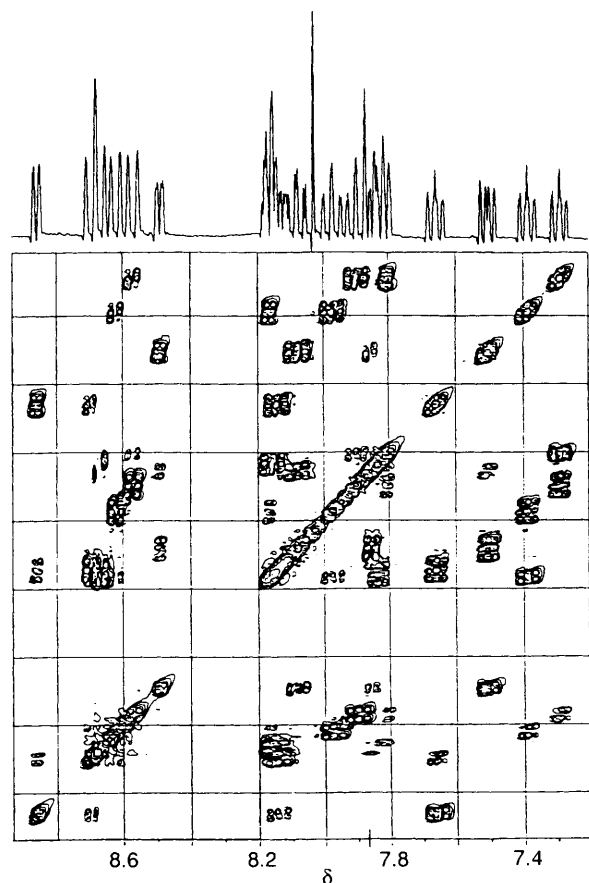
Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ru	9 602(1)	2 306(1)	2 925(1)	C(18)	6 181(19)	-967(9)	653(8)
Cl	12 389(3)	3 022(2)	2 734(1)	C(19)	7 971(20)	-289(11)	817(8)
N(1)	10 966(9)	3 665(5)	3 934(4)	C(20)	8 953(14)	620(7)	1 453(6)
C(1)	10 785(14)	4 609(6)	3 816(6)	N(5)	8 215(9)	2 979(5)	1 780(4)
C(2)	11 861(15)	5 512(8)	4 522(7)	C(21)	6 802(13)	3 346(7)	1 493(6)
C(3)	13 165(16)	5 458(9)	5 381(7)	C(22)	5 757(20)	3 380(11)	2 026(8)
C(4)	13 358(15)	4 498(9)	5 511(6)	C(23)	8 629(13)	3 088(7)	1 096(5)
C(5)	12 234(12)	3 576(7)	4 775(5)	N(6)	7 563(10)	3 518(5)	468(4)
N(2)	11 106(10)	1 785(6)	4 061(5)	N(7)	6 381(11)	3 687(6)	726(4)
C(6)	12 337(13)	2 559(7)	4 852(5)	N(8)	6 699(16)	4 457(9)	-818(7)
C(7)	13 508(18)	2 287(11)	5 656(7)	C(24)	7 608(14)	3 799(7)	-355(5)
C(8)	13 378(20)	1 250(13)	5 637(8)	C(25)	8 569(15)	3 404(8)	-582(6)
C(9)	12 204(20)	510(10)	4 878(9)	C(26)	8 650(19)	3 656(13)	-1 342(8)
C(10)	11 035(15)	781(8)	4 085(8)	C(27)	7 846(16)	4 342(10)	-1 862(7)
N(3)	7 240(10)	1 534(5)	3 034(5)	C(28)	6 865(19)	4 700(10)	-1 595(8)
C(11)	6 895(16)	1 857(8)	3 698(7)	P	812(5)	2 618(2)	7 163(2)
C(12)	5 201(17)	1 312(10)	3 692(9)	F(1)	1 810(19)	2 868(11)	8 258(7)
C(13)	3 868(18)	426(10)	3 029(10)	F(2)	2 650(20)	2 774(23)	7 265(10)
C(14)	4 149(14)	36(9)	2 390(9)	F(3)	-21(18)	2 446(12)	6 105(6)
C(15)	5 931(13)	638(7)	2 414(6)	F(4)	1 081(41)	3 726(10)	7 251(9)
N(4)	8 290(10)	906(5)	1 966(4)	F(5)	-1 087(23)	2 490(20)	7 029(11)
C(16)	6 496(13)	254(6)	1 791(6)	F(6)	335(30)	1 454(9)	7 121(3)
C(17)	5 378(16)	-696(8)	1 132(8)				

**Table 2** Selected bond lengths (Å) and angles ( $^\circ$ ) of  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]\text{PF}_6$  with e.s.d.s in parentheses

Cl-Ru	2.409(3)	N(1)-Ru	2.049(6)
N(2)-Ru	2.029(7)	N(3)-Ru	2.013(8)
N(4)-Ru	2.049(7)	N(5)-Ru	2.131(6)
C(21)-N(5)	1.36(1)	C(23)-N(5)	1.32(1)
C(22)-C(21)	1.53(2)	N(7)-C(21)	1.28(1)
N(6)-C(23)	1.33(1)	N(7)-N(6)	1.35(1)
C(24)-N(6)	1.42(1)	C(24)-N(8)	1.39(2)
C(28)-N(8)	1.38(2)	C(25)-C(24)	1.30(2)
C(26)-C(25)	1.33(2)	C(27)-C(26)	1.41(2)
C(27)-C(28)	1.33(2)		
N(1)-Ru-Cl	85.2(2)	N(2)-Ru-Cl	88.6(3)
N(2)-Ru-N(1)	78.8(3)	N(3)-Ru-Cl	173.3(2)
N(3)-Ru-N(1)	100.7(3)	N(3)-Ru-N(2)	89.3(3)
N(4)-Ru-Cl	95.1(3)	N(4)-Ru-N(1)	177.2(3)
N(4)-Ru-N(2)	98.4(3)	N(4)-Ru-N(3)	78.9(3)
N(5)-Ru-Cl	88.4(2)	N(5)-Ru-N(1)	97.4(3)
N(5)-Ru-N(2)	175.3(2)	N(5)-Ru-N(3)	94.0(3)
N(5)-Ru-N(4)	85.4(3)	C(1)-N(1)-Ru	126.2(5)
C(5)-N(1)-Ru	114.1(6)	C(6)-N(2)-Ru	115.4(6)
C(10)-N(2)-Ru	125.8(6)	C(11)-N(3)-Ru	125.3(5)
C(15)-N(3)-Ru	116.7(8)	C(16)-N(4)-Ru	115.4(8)
C(20)-N(4)-Ru	126.7(6)	C(21)-N(5)-Ru	136.3(7)
C(23)-N(5)-Ru	121.7(7)	C(23)-N(5)-C(21)	102.0(8)
C(22)-C(21)-N(5)	124.3(9)	N(7)-C(21)-N(5)	116(1)
N(7)-C(21)-C(22)	120(1)	N(6)-C(23)-N(5)	110(1)
N(7)-N(6)-C(23)	109.7(8)	C(24)-N(6)-C(23)	128(1)
C(24)-N(6)-N(7)	122.5(8)	N(6)-N(7)-C(21)	102.9(9)
C(28)-N(8)-C(24)	114(1)	N(8)-C(24)-N(6)	119(1)
C(25)-C(24)-N(6)	113.9(9)	C(25)-C(24)-N(8)	127(1)
C(26)-C(25)-C(24)	116(1)	C(27)-C(26)-C(25)	124(2)
C(27)-C(28)-N(8)	122(1)	C(28)-C(27)-C(26)	117(1)

pyridyltriazoles and monodentate triazole ligands do normally show substantially shorter Ru-N distances.<sup>8e,15</sup> The Ru-Cl distance of 2.409(3) Å is also in the range expected.<sup>16</sup> In the crystalline state, the plane of the pyridine ring of  $\text{L}^3$  lies at an angle of  $13.5^\circ$  to the plane of the triazole ring.

**Proton NMR Spectra.**—The usefulness of  $^1\text{H}$  NMR spectroscopy in the determination of the structure of ruthenium

**Fig. 3** 300 MHz Proton NMR spectrum between  $\delta$  9.0 and 7.0 of compound **5** in  $(\text{CD}_3)_2\text{CO}$ 

diimine complexes has been demonstrated.<sup>8,19</sup> The assignments of the resonances obtained for the compounds reported are given in the Experimental section. They were made using correlation spectroscopy (COSY) techniques and by comparison with other related compounds and with the free ligands. The spectrum of compound **5** is given in Fig. 3. The most important

question to be answered at this stage is the co-ordination mode of the pyridyltriazole ligands. As expected the spectra obtained for 4–7 are substantially different from those observed for the corresponding complexes containing the bidentate co-ordinated ligands.<sup>8a</sup> In the assignments made, the positions of the H<sup>6</sup> protons of the various pyridine rings enable the identification of most rings, as H<sup>6</sup> is very sensitive to interaction through space with neighbouring ligands, such as Cl<sup>-</sup> or triazole. Noteworthy also is the high-field resonance observed for compounds 3 and 6 for the methyl group on L<sup>3</sup>. This shift to higher field is consistent with the expected strong interaction of this group with the neighbouring bipy rings when co-ordination occurs *via* N<sup>2</sup> or N<sup>4</sup>.

From the resonances observed for the pyridine ring in the monodentate co-ordinated pyridyltriazole ligands it can be concluded that these ligands most likely are bound *via* the triazole ring. This assumption is based on the fact that for the pyridine ring in the monodentate co-ordinated L<sup>2</sup> and L<sup>3</sup> the resonance of the H<sup>5</sup> proton appears, as in the free ligand, as a quartet (see Fig. 3,  $\delta$  7.50). Also the position of the H<sup>3</sup> and H<sup>6</sup> protons is different. Due to the absence of steric interaction of H<sup>3</sup> with the triazole ring, no shift of this proton resonance to lower field is observed. Furthermore, because of interaction with the adjacent bipy rings (the diamagnetic anisotropic effect), H<sup>6</sup> is expected at much higher field when the pyridine ring is co-ordinated.<sup>8a</sup> It is also worth pointing out that one of the bipy H<sup>6</sup> protons appears at very low field, at about  $\delta$  10. This resonance is assigned to the proton interaction through space with a chloride or MeCN group rather than a bipy ligand. The similarity of the pyridine resonances observed for the monodentate L<sup>1</sup> complexes 4 and 7 suggests strongly that also in these compounds the pyridyltriazole ligands are bound *via* the triazole ring.

Another point of interest is the co-ordination mode of the triazole ring. The molecular structure of complex 6 has shown unambiguously that L<sup>3</sup> is bound *via* N<sup>4</sup> of the triazole ring. The similarity of the proton spectra of compounds 5 and 6 suggests that the same co-ordination mode is present in both. For the monodentate L<sup>1</sup> compounds no such direct evidence is available. A striking observation is however that according to the NMR spectra compound 4 can be obtained by photochemical as well as thermal means. The pyridine resonances of the pyridyltriazole ligand for this compound strongly suggest a triazole-based co-ordination. The monodentate co-ordination mode observed for L<sup>2</sup> and L<sup>3</sup> suggests that in the thermally produced products the co-ordination site that offers least steric hindrance is favoured. It also seems clear that, when co-ordination would have to take place *via* one of the chelating sites, bidentate co-ordination results. This is particularly clear from experiments carried out with the ligands L<sup>4</sup> and L<sup>5</sup> (see Fig. 1). These ligands only contain nitrogen atoms at chelating sites, and as a result only bidentate co-ordination was obtained with these ligands under similar conditions. Because of

these observations it is suggested that that in 4 co-ordination occurs *via* the N<sup>1</sup> atom. This is a very important observation because it suggests that, in the photochemically obtained compound 4, co-ordination of the central ruthenium atom to the triazole ring has changed from the chelating N<sup>2</sup> position to the N<sup>1</sup> atom.

For compound 7 a resonance at  $\delta$  2.55 clearly indicates that MeCN is co-ordinated to the ruthenium(II) centre, as free acetonitrile is found at  $\delta$  1.95.<sup>20</sup> In particular the position of H<sup>3</sup> ( $\delta$  7.80, at rather high field due to absence of steric hindrance from other protons), H<sup>6</sup> ( $\delta$  8.69, at rather low field as this proton does not interact with bipy rings), and methyl resonances ( $\delta$  4.12) of the pyridyltriazole ligand suggest that the ligand is co-ordinated to the metal centre *via* the triazole ring. It is assumed that also in this case co-ordination is *via* the N<sup>1</sup> atom. The fact that photolysis of [Ru(bipy)<sub>2</sub>(L<sup>4</sup>)]<sup>2+</sup> in MeCN does not yield any monodentate intermediates supports this suggestion.

**Electronic and Redox Properties.**—The electronic and redox properties of compounds 1–7 are given in Table 3. As for other ruthenium(II) diimine compounds the lowest-energy absorption is assigned to a metal-to-ligand charge-transfer transition.<sup>8,12</sup> The position of this band for compounds 4–6 is in agreement with the presence of a RuN<sub>5</sub>Cl moiety and the shift observed by comparison with the chelating analogues is as expected.<sup>13</sup> This co-ordination mode and, in particular, the presence of the chloride ion, is also confirmed by the emission energies and the low oxidation potential observed. Both the emission and the ligand-based reduction processes are most likely bipy based.<sup>8,13</sup> The data do not however discriminate between the different co-ordination modes possible. Table 3 illustrates the similarity between the electronic and redox properties of compounds 1 and 7. On the basis of the ligands involved this resemblance is not unexpected. Because of the presence of small amounts of 1 (less than 5%) in the samples obtained for 7, exact absorption coefficients could not be obtained. The presence of 1 also caused problems in the measurement of emission spectra for 7. The only emission obtained was a very weak signal that was attributed to 1. From UV/VIS spectra taken during the photolysis of 1 in MeCN it is estimated that the absorption coefficient at  $\lambda_{\max}$  of 7 is about 60% of that of compound 1.

**Photochemical Experiments.**—Compounds 1–3 were photolysed in both pure MeCN and MeCN containing 0.01 mol dm<sup>-3</sup> LiCl. The purpose of these experiments was the isolation of intermediates containing monodentate co-ordinated ligands. It was anticipated that the presence of the pyridyltriazole ligands would give rise to monodentate species since these ligands contain two different co-ordination sites; one pyridine- and one triazole-based.

In both MeCN and in MeCN–LiCl the largest concentrations of intermediate species were obtained for the photolysis of compound 1. The photolyses of compounds 2 and 3 yield similar

Table 3 Electronic and redox properties of compounds 1–7

Compound	Absorption maximum <sup>a</sup> $\lambda$ /nm (log $\epsilon$ )	Emission maxima <sup>b</sup> /nm		<i>E</i> <sup>c</sup> /V vs. SCE	
		300 K <sup>a</sup>	77 K <sup>b</sup>	Ru <sup>II</sup> –Ru <sup>III</sup> oxidation	Ligand-based reductions
1	440 (4.16)	600	584	1.21	–1.42, –1.64
2	420 (4.03)	—	560	1.35	–1.42, –1.63
3	433 (4.00)	590	580	1.36	–1.36, –1.56
4	508 (3.96)	710	655	0.66	–1.34
5	500 (3.97)	710	655	0.78	–1.53
6	502 (3.97)	680	658	0.79	–1.45
7	440 (—)	<i>d</i>		1.16	Adsorption

<sup>a</sup> Obtained in MeCN; values  $\pm$  2 nm for absorption spectra,  $\pm$  5 nm for emission spectra. <sup>b</sup> Obtained in ethanol, values  $\pm$  5 nm. <sup>c</sup> Obtained in MeCN–0.1 mol dm<sup>-3</sup> NEt<sub>4</sub>ClO<sub>4</sub> using differential pulse polarography; values  $\pm$  0.02 V, all redox processes are reversible. <sup>d</sup> See text.

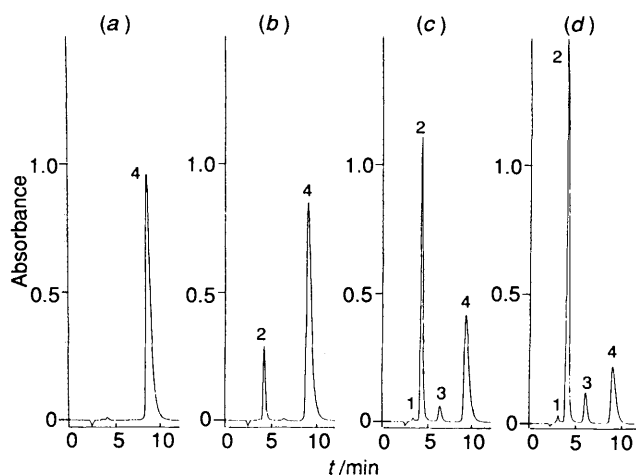


Fig. 4 The HPLC traces taken during the photolysis of compound **1** in MeCN. Photolysis times: (a) 0, (b) 60, (c) 360 and (d) 660 s. Flow rate  $2.0 \text{ cm}^3 \text{ min}^{-1}$ , mobile phase MeCN–water (80:20) containing  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ , detection wavelength 280 nm. For peak numbering see text

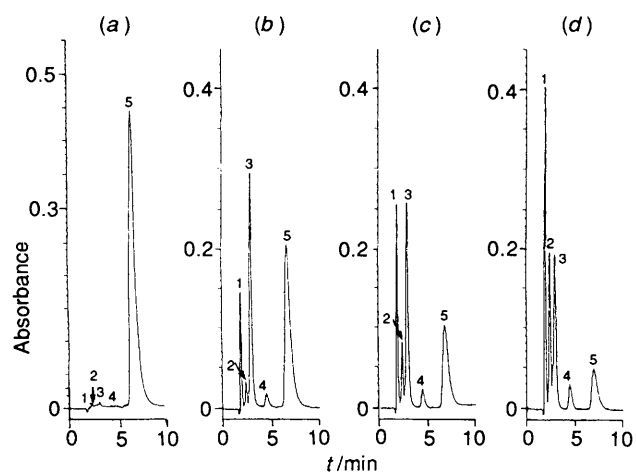
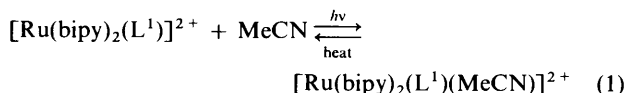


Fig. 5 The HPLC traces taken during the photolysis of compound **1** in MeCN containing  $0.01 \text{ mol dm}^{-3} \text{ LiCl}$ . Photolysis times: (a) 0, (b) 200, (c) 400 and (d) 700 s. Other details as in Fig. 4

results in that the same types of intermediates and final products are obtained. However, the concentrations of the intermediates of interest in this work are considerably lower. Therefore, only the results obtained for compound **1** are discussed in detail. The UV/VIS spectra taken during the photolysis of **1** in both MeCN and MeCN–LiCl do not show isosbestic points, clearly indicating the formation of more than one photoproduct. During the photolysis of **1** in MeCN the absorption maximum of the reaction mixture shifts from 450 to 425 nm. To investigate these reactions further an HPLC analysis of the photolysis was carried out. Traces taken during the photolysis of **1** in MeCN are depicted in Fig. 4. From the HPLC analysis it is clear that upon photolysis of **1** (peak 4) three main products are formed. The first one, peak 2, has a retention time of 4.05 min and an absorption maximum at 445 nm. The final product, peak 3, obtained as the sole product after about 1 h of photolysis, has a retention time of 6.05 min and an absorption maximum of 425 nm. The third species, peak 1, retention time 3.01 min was identified as free ligand. The UV/VIS spectra were obtained using a diode-array detector and the solvent is therefore the mobile phase. The final product was identified as  $[\text{Ru}(\text{bipy})_2(\text{MeCN})_2]^{2+}$ , by comparison with an authentic sample. This compound is also the expected final photoproduct. From the fact that no free ligand is formed during the formation of peak 2, and from the absorption maximum of 445 nm, this species is identified as  $[\text{Ru}(\text{bipy})_2(\text{L}^1)(\text{MeCN})]^{2+}$ , in which the pyridyl-

triazole ligand is bound in a monodentate fashion. This assumption has been substantiated by the proton NMR spectra obtained for this compound (see above).

Further evidence about the nature of the intermediate was obtained by a study of its thermal properties, e.g. the back reaction in equation (1). The compound was heated at  $80^\circ \text{C}$  in



$\text{CD}_3\text{CN}$  and proton NMR spectroscopy clearly showed the formation of **1** as the sole product. The resonances observed for **7** disappear and are replaced by signals that can be attributed to **1**,<sup>8a</sup> also the resonance of co-ordinated MeCN is lost upon heating. Preliminary investigations on the kinetics and thermodynamics of this reaction suggest that it follows first-order kinetics with a rate constant of  $(2 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$  at  $80^\circ \text{C}$ . The activation energy of the reaction in MeCN, obtained from measurements carried out over the range  $70\text{--}88^\circ \text{C}$ , is  $110 \pm 10 \text{ kJ mol}^{-1}$  and the entropy change is close to zero.

Further photochemical experiments were carried out with complex **7** in both methanol and acetone. Very surprisingly, HPLC and UV/VIS analysis shows clearly that upon photolysis of **7** in these solvents the original starting material compound **1** is formed as the only product. This suggests that while upon photolysis of **7** in MeCN decomposition occurs, with the formation of  $[\text{Ru}(\text{bipy})_2(\text{MeCN})_2]^{2+}$ , in solvents that are weak ligands, such as acetone and methanol, photochemically induced ring closure is observed.

Photolysis of complex **1** in MeCN–LiCl shows a more complicated picture. Again UV/VIS spectra taken during the photolysis do not show isosbestic points. The HPLC traces taken during the photolysis are shown in Fig. 5. In the initial stages of the reaction (up to  $t = 170 \text{ s}$ ) the main product obtained is peak 3, which has a retention time of 3.01 min and an absorption maximum of 445 nm. This species was identified as compound **7**. The formation of this compound reaches a maximum at about 540 s and subsequently decreases. Another intermediate, peak 1, with a retention time of 1.95 min and absorption maxima of 500 and 340 nm, is also formed early in the reaction. A small amount of this material was isolated from a preparative-scale experiment and NMR spectroscopy has very surprisingly shown this material to be identical to **4**. Other more conventional products obtained are  $[\text{Ru}(\text{bipy})_2(\text{MeCN})_2]^{2+}$ , peak 4, retention time 4.44 min,  $\lambda_{\text{max}}$  425 nm, and  $[\text{Ru}(\text{bipy})_2(\text{MeCN})\text{Cl}]^+$ , peak 2, retention time 2.42 min and  $\lambda_{\text{max}}$  475 nm. These products were identified by comparison with authentic samples. On the basis of the peak areas obtained for the different products a distribution of the products obtained during the photolysis can be obtained (Fig. 6).

## Conclusion

The isolation and characterisation is described of a series of complexes containing potentially chelating pyridyltriazole ligands bound in a monodentate fashion. To obtain these compounds thermal as well as photochemical methods were employed. One of the interesting results obtained is that for both the thermally as well as the photochemically obtained products the monodentate co-ordinated ligands are not bound through the  $\text{N}^2$  nitrogen of the triazole ring. The products obtained from thermal methods show clearly that the chelate effect is not always an overriding consideration. Under the conditions reported, where the second chloride atom is strongly co-ordinated to the metal centre, steric considerations prevail. The co-ordination mode observed is particularly surprising for the photochemically obtained products  $[\text{Ru}(\text{bipy})_2(\text{L}^1)\text{Cl}]^+$  and  $[\text{Ru}(\text{bipy})_2(\text{L}^1)(\text{MeCN})]^{2+}$ . Clearly a photochemically induced slippage of the co-ordination bond from the  $\text{N}^2$  to the  $\text{N}^1$  atom of the ligand  $\text{L}^1$  occurs. To our knowledge this the first

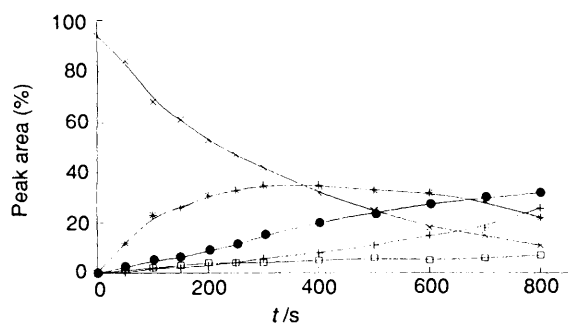


Fig. 6 Variation with time of the concentration of the various photoproducts formed during the photolysis of compound **1** in MeCN containing  $0.01 \text{ mol dm}^{-3}$  LiCl. Products:  $\times$ ,  $[\text{Ru}(\text{bipy})_2(\text{L}^1)]^{2+}$ ;  $*$ ,  $[\text{Ru}(\text{bipy})_2(\text{L}^1)(\text{MeCN})]^{2+}$ ;  $\bullet$ ,  $[\text{Ru}(\text{bipy})_2(\text{L}^1)\text{Cl}]^+$ ;  $\square$ ,  $[\text{Ru}(\text{bipy})_2-(\text{MeCN})_2]^{2+}$ ;  $+$ ,  $[\text{Ru}(\text{bipy})_2(\text{MeCN})\text{Cl}]^+$

time that such a reversible switching of the co-ordination mode is observed for triazole compounds. Perhaps even more surprising is the fact that this change in co-ordination site can be reversed not only by heating the compound but also by photochemical means. Normally photolysis of ruthenium diimine complexes leads to loss of ligands; the regeneration of a bidentate co-ordination mode has not so far been observed. The crystal structure of  $[\text{Ru}(\text{bipy})_2(\text{L}^3)\text{Cl}]\text{PF}_6$  shows that the metal to ligand distances are little affected by the unusual co-ordination mode of the triazole ligand, all distances being within the ranges expected.

In a preliminary investigation the compound  $[\text{Ru}(\text{bipy})_2(\text{L}^1)-(\text{MeCN})]^{2+}$  was proposed as the first example of a photochemically produced intermediate where one of the ligands is bound in a monodentate fashion. Our results confirm the monodentate co-ordination of the pyridyltriazole. However the co-ordination observed is not through  $\text{N}^2$  and the products obtained are therefore specific for triazole ligands, as slippage of the co-ordination to  $\text{N}^1$  occurs. Overall the results obtained show that ruthenium diimine complexes containing pyridyltriazoles exhibit quite unexpected and novel photochemical processes and although the results obtained are specific to triazole compounds they are of general importance for the understanding of photochemical processes in inorganic chemistry.

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