Letter

# Metal-assisted electrocyclic reaction in a C=N–N=C–C=N system

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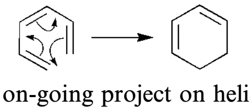
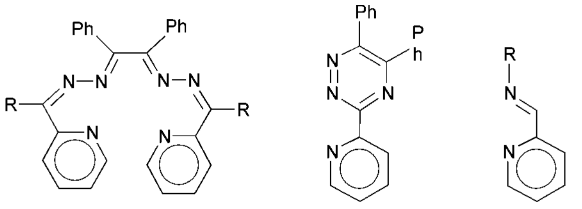
**In a reaction with *cis*-Ru(phen)$_2$Cl$_2$, the 1 : 2 condensate of benzil dihydrazone and 2-formylpyridine or 2-acetylpyridine is found to undergo an electrocyclic rearrangement to yield the cation [Ru(phen)$_2${5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine}]$^{2+}$, which has been isolated as its hexafluorophosphate salt and characterised by X-ray crystallography.**

It is known that 1,3,5-trienes undergo an electrocyclic rearrangement to yield 1,3-cyclohexadienes [reaction (1)]; the reaction, in general, occurs thermally.[1] Such reactions are conceivable for analogous systems containing imino nitrogen(s), but this has never been demonstrated. Herein, for the first time, we report an electrocyclic rearrangement for a system containing a C=N–N=C–C=N moiety. The rearrangement is, however, assisted by ruthenium(II).



(1)

As a part of our on-going project on helical metal complexes,[2,3] we wanted to prepare a spiral complex of ruthenium(II) with the ligands L and MeL. For this purpose, L and MeL have been reacted with *cis*-Ru(phen)$_2$Cl$_2$ · 2H$_2$O, where phen = 1,10-phenanthroline.



L: R = H; MeL: R = Me L′ L″

The ligands L and MeL were synthesised by condensing one mol of benzil dihydrazone with two mol of 2-formylpyridine and 2-acetylpyridine, respectively, in anhydrous methanol. The structure of one of the ligands, L, has been determined by X-ray crystallography (Fig. 1). The two pyridine moieties are found on opposite sides of the N3–C1–C2–N6 fragment, giving rise to a double helix. However, the space group is centrosymmetric, indicating that the ligand crystallises as a racemate. The main source of the helical twist in L is the torsion angle of −99.5(3)° about the bonds N3–C1–C2–N6. For comparison, the O=C–C=O dihedral angle in benzil in the solid state is 70°.[4] In L, the C31–C1–N3–N4–C5–C11 and C21–C2–N6–N7–C8–C41 moieties are approximately planar with RMS deviations of the contributing atoms of 0.07 and 0.02 Å, respectively, indicative of significant conjugation.

It is found that when *cis*-Ru(phen)$_2$Cl$_2$ · 2H$_2$O is refluxed with L or MeL in a 1 : 1 water–methanol mixture, [Ru(phen)$_2$L′](PF$_6$)$_2$ · H$_2$O (**1**) can be isolated from the reaction mixture by adding NH$_4$PF$_6$ [reaction (2)].

$$cis\text{-Ru(phen)}_2\text{Cl}_2 + \text{L or MeL} \xrightarrow[\text{aq. MeOH}]{\Delta} [\text{Ru(phen)}_2\text{L}']^{2+} \qquad (2)$$

The structure of the cation in **1**, as determined by X-ray crystallography, is shown in Fig. 2. The space group is centrosymmetric, indicating that the complex crystallises as a racemate. The metal has a slightly distorted octahedral N$_6$ coordination sphere. The Ru–N bond lengths for the two phen ligands lie in the range 2.036(11)–2.075(12) Å; in contrast, for L′, the Ru–N11 bond at 1.990(8) Å is the shortest and Ru–N41 is the longest at 2.088(7) Å. Incidentally, **1** provides the first example of a structurally characterised ruthenium(II) complex of a pyridyltriazine system. However, [Ru(bpy)$_2$L′](PF$_6$)$_2$ · H$_2$O · (CH$_3$)$_2$CO, where bpy = 2,2′-bipyridine, a complex very similar to **1**, has been reported earlier by Reedijk and co-workers. They synthesised this complex by reacting preformed L′ with *cis*-Ru(bpy)$_2$Cl$_2$ · 2H$_2$O.[5] it has previously been shown by others that the ligand L′ can be used for quantitative estimation of Ru(II) and Fe(II).[6,7]

A tentative mechanism for reaction (2) is suggested in Scheme 1. This seems to be a case of electrocyclic rearrangement in L or MeL in the chelated mode. In stage I of Scheme 1, L or MeL is proposed to first bind ruthenium(II) in a mode similar to that known[8] for L″ and then reorient itself to yield a geometry conducive for the cyclisation. The driving force for

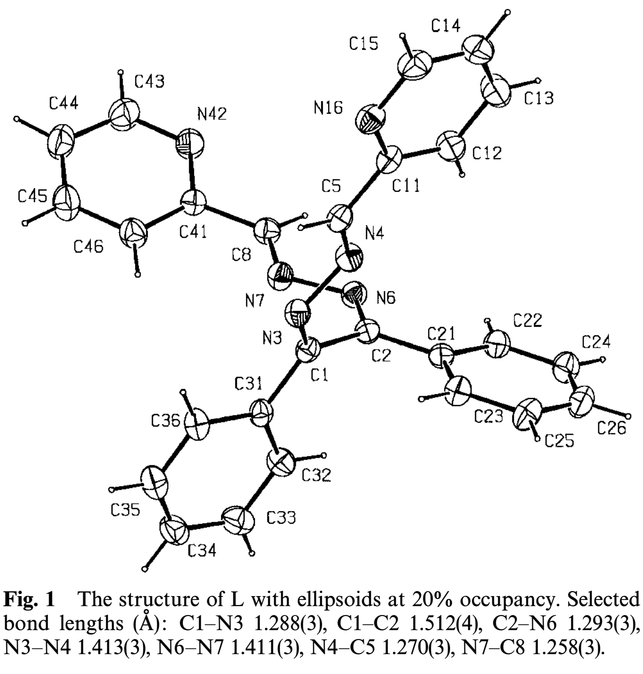


**Fig. 1** The structure of L with ellipsoids at 20% occupancy. Selected bond lengths (Å): C1–N3 1.288(3), C1–C2 1.512(4), C2–N6 1.293(3), N3–N4 1.413(3), N6–N7 1.411(3), N4–C5 1.270(3), N7–C8 1.258(3).

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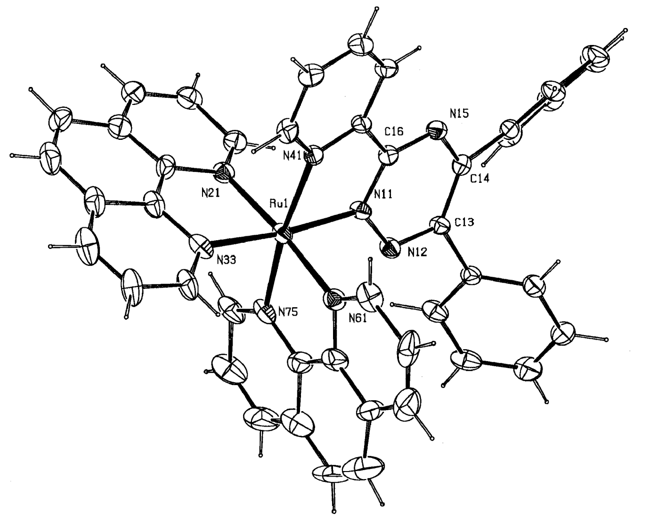
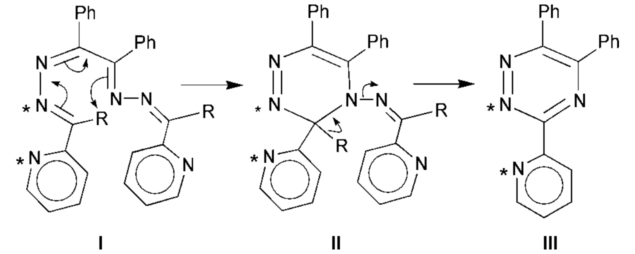


**Fig. 2** The structure of the cation in **1** with ellipsoids at 20% occupancy. Selected bond lengths (Å) and angles (°): N11–N12 1.365(10), Ru1–N11 1.990(8), Ru1–N41 2.088(7), Ru1–N21 2.036(11), Ru1–N33 2.075(12), Ru1–N61 2.036(12), Ru1–N75 2.065(10), N11–Ru1–N41 78.6(3), N61–Ru1–N75 79.3(5), N21–Ru1–N33 81.2(5), N21–Ru1–N61 174.7(4), N11–Ru1–N33 173.2(4), N75–Ru1–N41 172.2(4).



**Scheme 1** A proposed mechanism for reaction (2); the N atoms marked by asterisks are bound to Ru(II).

the conversion of stage II to stage III in Scheme 1 seems to be the tendency to acquire aromaticity. Scheme 1 indicates that in reaction (2), in the case of L, a Schiff base of 2-formylpyridine and $NH_3$ (R = H in L″) and in the case of MeL, a Schiff base of 2-acetylpyridine and $CH_3NH_2$, are also produced along with $[Ru(phen)_2L']^{2+}$. However, after isolation of **1** from the filtrate we could only obtain 2-formylpyridine (in the case of L) or 2-acetylpyridine (in the case of MeL) in 12–15% yield after work-up. This shows that under the conditions employed, the Schiff bases generated in reaction (2) are hydrolysed.

We have tried to prepare L′ from L and MeL thermally. Heating of the ligands at 10 °C above their melting points for 1 h leaves them unchanged. However, the ligands decompose when heated at 200 °C for 15 min. Thus, the metal ion here plays a distinct role in bringing about the observed electrocyclic rearrangement.

## Experimental

### Syntheses

**Synthesis of L.** Benzil dihydrazone (1.87 g, 7.86 mmol), synthesised by a reported procedure,[9] was dissolved in 30 ml of anhydrous methanol. To this colourless solution, 1.5 ml (15.72 mmol) of freshly distilled 2-formylpyridine was added. The resulting light yellow mixture was refluxed for 6 h, maintaining a dry atmosphere. Then it was slowly cooled to room temperature under dry conditions to yield large yellow cuboid crystals of L. The crystals were suitable for X-ray crystallography. Yield, 2.33 g (70%); mp 159–162 °C. Anal. found (calc.): C, 74.87 (74.98); H, 4.78 (4.84); N, 20.27 (20.18%). UV/VIS ($CH_2Cl_2$) $\lambda_{max}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$): 306 (53 400).

**Synthesis of MeL.** This ligand was prepared by a procedure exactly the same as that for L by starting with 1.87 g (7.86 mmol) of benzil dihydrazone dissolved in 30 ml of anhydrous methanol and 1.8 ml (15.72 mmol) of freshly distilled 2-acetylpyridine to obtain yellow micro crystals of MeL. Yield, 2.76 g (80%); mp 135–138 °C. Anal. found (calc.): C, 75.59 (75.64); H, 5.33 (5.45); N, 18.93 (18.91%). UV/VIS ($CH_2Cl_2$) $\lambda_{max}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$): 280 (43 600).

**$[Ru(phen)_2(L')](PF_6)_2\cdot H_2O$ (1).** *cis*-$Ru(phen)_2Cl_2\cdot 2H_2O$ (0.28 g, 0.5 mmol), synthesised by a reported procedure,[10] was dissolved in 25 ml of a degassed 1 : 1 methanol–water mixture. To this red solution, 0.21 g (0.5 mmol) of L [or 0.22 g (0.5 mmol) of MeL] was added and the resulting mixture was refluxed under $N_2$ atmosphere for 6 h. Then the orange–red reaction mixture was cooled to room temperature and 0.5 g of $NH_4PF_6$ dissolved in 5 ml of water was added dropwise with constant stirring. The mixture was left in air for 30 min. The reddish compound that precipitated was filtered, washed with 15 ml of diethyl ether and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a dichloromethane–*n*-hexane mixture. Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Yield, 0.35 g (65%). Anal. found (calc.): C, 49.10 (48.91); H, 3.13 (2.98); N, 10.34 (10.37%). $\Lambda_M$ ($CH_3OH$): 176 Ω$^{-1}$ cm$^2$ mol$^{-1}$ (1 : 2 electrolyte). UV/VIS ($CH_2Cl_2$) $\lambda_{max}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$): 475 (18 900), 427 (17 700), 291 (52 800). $^1$H NMR (300 MHz, $CD_2Cl_2$, TMS) $\delta_H$: 6.91 (dd, 2 H, $J$ = 1.3 and 7.8), 7.17 (t, 2 H, $J$ = 7.6), 7.32–7.40 (m, 3 H), 7.48–7.63 (m, 3 H), 7.68 (dd, 2 H, $J$ = 1.3 and 7.9), 7.76–7.83 (m, 2 H), 7.87–7.97 (m, 3 H), 8.10–8.22 (m, 6 H), 8.36 (dd, 1 H, $J$ = 1.1 and 5.2), 8.50 (dd, 1 H, $J$ = 1.2 and 8.2), 8.56–8.64 (m, 4 H) and 8.88 (d, 1 H, $J$ = 7.9 Hz).

### X-ray crystallography

The data were collected with Mo-Kα radiation using the MARresearch Image Plate System at 293(2) K. The non-hydrogen atoms were refined anisotropically and remaining atoms isotropically. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms bonded to the water molecules were not included. The structures were refined on $F^2$ using SHELXL-93.[11] Final $R$ values: for L with observed data $I > 2\sigma(I)$, $R_1 = 0.0695$, $wR_2 = 0.1867$ and for all data $R_1 = 0.1218$, $wR_2 = 0.2214$; for **1** with observed data $I > 2\sigma(I)$, $R_1 = 0.1137$, $wR_2 = 0.2809$ and for all data $R_1 = 0.2252$, $wR_2 = 0.3301$. The crystals of **1** were of poor quality and gave irregular spot shapes, which accounts for the relatively high $R$ values.

**Crystal data.** $C_{26}H_{20}N_6$ (L): $M_w = 416.48$, monoclinic, space group $P2_1/c$, $a = 10.404(14)$, $b = 18.94(2)$, $c = 1.673(14)$ Å, $\beta = 105.80(1)°$, $U = 2213(5)$ Å$^3$, $Z = 4$, $\mu = 0.078$ mm$^{-1}$, 7894 reflections collected, 4337 unique, $R$(int) = 0.0375. $C_{44}H_{32}F_{12}N_8OP_2Ru$ (**1**): $M_w = 1079.79$, monoclinic, space group $P2_1/n$, $a = 13.785(15)$, $b = 16.860(19)$, $c = 20.91(2)$ Å, $\beta = 102.04(1)°$, $U = 4753(9)$ Å$^3$, $Z = 4$, $\mu = 0.488$ mm$^{-1}$, 20 082 reflections collected, 7954 unique, $R$(int) = 0.0754.

CCDC reference number 440/225. See http://www.rsc.org/suppdata/nj/b0/b006547l/ for crystallographic files in .cif format.

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