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Metallo-Organic Domino Reactions: C−H versus C−C Bond Breaking

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Abstract: HL and MeL are prepared by condensing benzil dihydrazone with 2-formylpyridine and 2-acetylpyridine, respectively, in 1:2 molar proportions. While in a reaction with $[Ru(C_6H_6)Cl_2]_2$, HL yields the cation $[Ru(C_6H_6)\{5,6\text{-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine}\}Cl]^+$, MeL gives the cation $[Ru(C_6H_6)(MeL)Cl]^+$. Both the cations are isolated as their hexafluorophosphate salts and characterised by X-ray crystallography. In the case of HL, double domino electrocyclic/elimination reactions are found to occur. The electrocyclic reaction occurs in a C=N−N=C−C=N fragment of HL and the elimination reaction involves breaking of a C−H bond of HL. Density functional calculations on model complexes indicate that the identified electrocyclic reaction is thermochemically as well as kinetically feasible for both HL and MeL in the gas phase. For a double domino reaction, similar to that operative in HL, to occur for MeL, breaking of a C−C bond would be required in the elimination step. Our model calculations show the energy barrier for this elimination step to be much higher (329.1 kJ mol^{-1}) for MeL than that for HL (96.3 kJ mol^{-1}). Thus, the domino reaction takes place for HL and not for MeL. This accounts for the observed stability of $[Ru(C_6H_6)(MeL)Cl]^+$ under the reaction conditions employed.

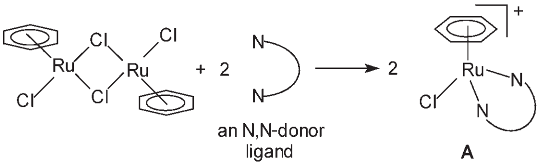
Keywords: arene complexes · domino reactions · N ligands · ruthenium

Introduction

The usual procedure for the synthesis of organic compounds is the stepwise formation of the individual bonds in the target molecule. But, in an emerging efficient synthetic strategy several bonds are formed in one sequence without isolating the intermediates, changing the reaction conditions or adding reagents/catalysts.[1–6] In such a sequence, if the first reaction is triggered, subsequent reactions seem to follow automatically. This cascade of reactions in a single pot are called domino reactions. In nature, domino reactions are quite common. But these cannot be compared directly with those in a flask because of the involvement of multienzymes which can catalyse different steps. Anyway, such reactions have not yet been properly identified in inorganic chemistry. Herein, we report the characterisations of some metallo-organic domino reactions.

Results and Discussion

Reaction of a bidentate N,N-donor ligand with $[Ru(C_6H_6)Cl_2]_2$ in a 2:1 molar ratio generally gives rise to mononuclear ruthenium(II) benzene complexes of type **A** [Eq. (1)].[7–11] In attempts to prepare helical dinuclear ruthenium(II) benzene complexes as a part of our on-going project on helical metal complexes,[12–15] we reacted $[Ru(C_6H_6)Cl_2]_2$ with the helical tetradentate N-donor ligands RL (R is H or Me). The X-ray crystal structure of the ligand HL has been reported earlier by us.[16]



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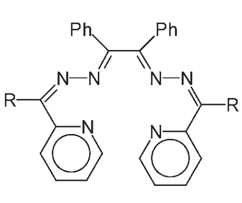
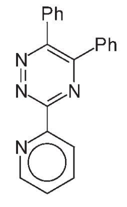
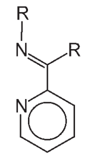


RL

R = H: HL
R = Me: MeL

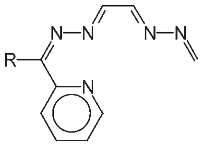


L'



RL''

R = H: HL''
R = Me: MeL''



RL'''

R = H: HL'''
R = Me: MeL'''

Refluxing of $[Ru(C_6H_6)Cl_2]_2$ with HL in methanol in equimolar proportions in the presence of NH_4PF_6 leads to the isolation of a yellow compound $[Ru(C_6H_6)(L')Cl]PF_6$ ($[\mathbf{1}]PF_6$). Direct diffusion of petroleum ether into a dilute acetone solution of $[\mathbf{1}]PF_6$ yields yellowish-orange single crystals of $[\mathbf{1}]PF_6{\cdot}1.5$(acetone) which slowly lose the solvent molecules. This compound crystallises in the monoclinic space group $P2_1/n$ with one $[Ru(C_6H_6)(L')Cl]^+$ cation, a $[PF_6]^-$ anion and two molecules of acetone in the asymmetric unit. One acetone has full occupancy while the other is refined with a model in which each atom is assigned 50% occupancy. The structure of the cation $[Ru(C_6H_6)(L')Cl]^+$ is shown in Figure 1. The ruthenium ion exhibits the usual piano-stool conformation common to ruthenium(II) arene compounds of type **A** [vide Eq. (1)] with little variation in the Ru–C distances (2.165–2.200 Å). The Ru–Cl distance, 2.3797(10) Å, is at the lower end of the typical range (2.36–2.44 Å) of ruthenium chloride bond lengths in ruthenium(II) arene compounds reported in the Cambridge Crystallographic Database. The Ru–N distances, 2.053(3) and 2.090(3) Å, are similar to those observed in several ruthenium(II) complexes of type **A**. The bite angle at the metal is 70.07(11)°. The two heterocyclic rings bonded to ruthenium are essentially coplanar while the interplanar angles between the phenyl rings and the triazine ring are 36.2 and 45.3°.

When $[Ru(C_6H_6)Cl_2]_2$ is refluxed with MeL in methanol in a 1:1 molar ratio in the presence of NH_4PF_6, a yellow compound $[Ru(C_6H_6)(MeL)Cl]PF_6{\cdot}4H_2O$ ($[\mathbf{2}]PF_6{\cdot}4H_2O$) is obtained. Upon direct diffusion of petroleum ether into a dilute solution of $[\mathbf{2}]PF_6{\cdot}4H_2O$ in acetone, yellowish-orange single crystals of $[\mathbf{2}]PF_6{\cdot}$acetone are obtained. This compound crystallises in the triclinic space group $P\bar{1}$ with two $[Ru(C_6H_6)(MeL)Cl]^+$ cations in the asymmetric unit. The two crystallographically unique cations are chemically closely similar. The asymmetric unit also contains two molecules of acetone and two $[PF_6]^-$ anions, one of which is disordered. A disordered model was refined in which the two axial sites were common to both components and each of the four equatorial fluorines occupied two sites in a 60:40 ratio. The structure of the cation $[Ru(C_6H_6)(MeL)Cl]^+$ is shown in Figure 2. The geometry at ruthenium is essentially similar to that described for $[Ru(C_6H_6)(L')Cl]^+$. The Ru–C distances cover a range of 2.177(3)–2.203(3) Å. The two independent Ru–Cl distances are 2.3865(6) and 2.3794(6) Å. The organic ligand binds ruthenium(II) at two N atoms and the other N-donor atoms remain uncoordinated (Figure 2). Bond lengths to the pyridyl nitrogen atoms are 2.074(2) and 2.073(2) Å, while those to N(2) and N(8) are 2.0973(2) and

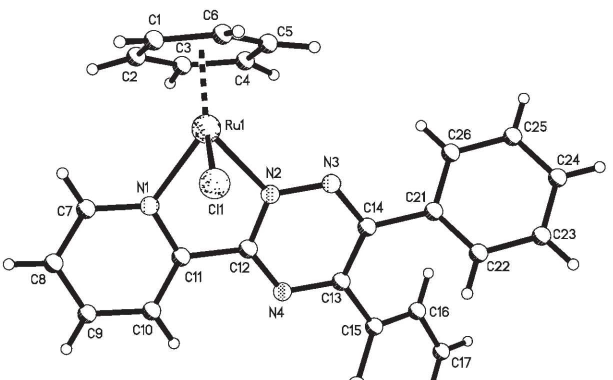


Figure 1. A view of the structure of the cation $[Ru(C_6H_6)(L')Cl]^+$ (**1**). Selected bond lengths [Å] and angles [°]: Ru1–N1 2.090(3), Ru1–N2 2.053(3), Ru1–Cl1 2.3797(10), Ru1–C1 2.199(4), Ru1–C2 2.197(4), Ru1–C3 2.192(4), Ru1–C4 2.165(4), Ru1–C5 2.200(4), Ru1–C6 2.180(4) Å; N1-Ru1-N2 77.07(11), N1-Ru1-Cl1 83.58(9), N2-Ru1-Cl1 85.29(9).

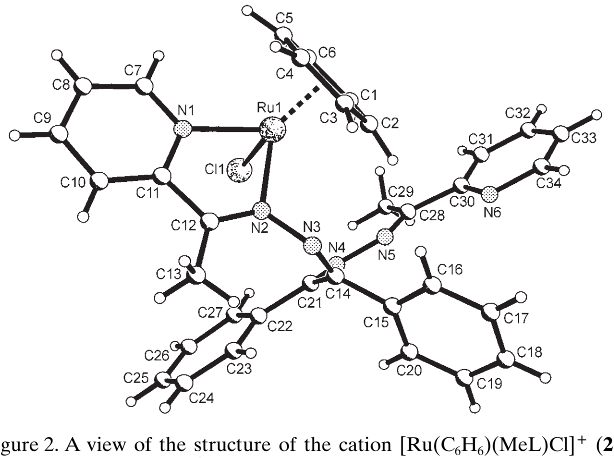
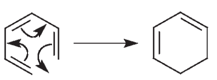


Figure 2. A view of the structure of the cation $[Ru(C_6H_6)(MeL)Cl]^+$ (**2**). Selected bond lengths [Å], bond angles [°] and torsion angles [°] in one of the two independent cations in the asymmetric unit: Ru1–N1 2.074(2), Ru1–N2 2.0973(19), Ru1–Cl1 2.3865(6), Ru1–C1 2.200(2), Ru1–C2 2.199(2), Ru1–C3 2.177(3), Ru1–C4 2.186(3), Ru1–C5 2.191(3), Ru1–C6 2.197(2); N1-Ru1-N2 76.07(8), N1-Ru1-Cl1 85.95(6), N2-Ru1-Cl1 88.98(5), C12-N2-N3-C14 117.6(3), N2-N3-C14-C21 −6.5(3), N3-C14-C21-N4 114.4(3), C14-C21-N4-N5 −2.3(3), C21-N4-N5-C28 −171.2(3), N4-N5-C28-C30 −176.1(2), N5-C28-C30-C31 −170.4(2).

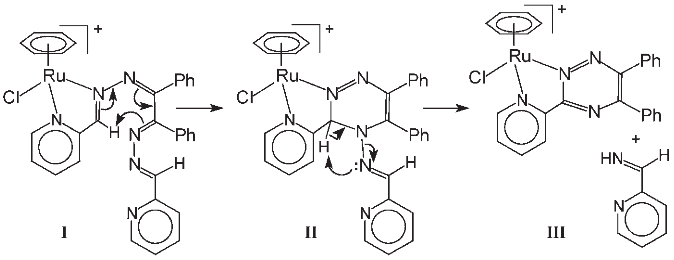
2.101(2) Å. Although these differences are statistically significant, they are no more than those seen between the two equivalent Ru–N bonds in $[Ru(C_6H_6)(L')Cl]^+$. The pendant portions of the two ligands exhibit a significant non-planar torsion about the central C–C bond, (N(3)-C(14)-C(21)-N(4): 114.4(3)° and N(9)-C(48)-C(55)-N(10): 117.4(3)°) but are otherwise substantially planar (selected torsion angles in these portions of the ligands are given in the legend to Figure 2).

We now summarise the results of our experiments. In organic chemistry, there is a very important class of reactions known as electrocyclic reactions. The definition was given by Woodward and Hoffman in the 1960s.[17] A text book example of this class of reactions is given by Equation (2).



(2)

That such reactions are also possible in C=C–C=C–C=N systems is known from experiment,[18] and have been studied in detail theoretically.[19–22] In our reaction of $[Ru(C_6H_6)Cl_2]_2$ with HL, we seem to have a case of a metal-assisted electrocyclic reaction in a C=N–N=C–C=N sequence. In the proposed mechanism (Scheme 1), a mononuclear ruthenium(II) benzene complex of type **A** with HL binding in a bidentate mode is presumed to form first. After binding to the metal, the ligand HL reorients itself to a conformation conducive for electrocyclic reaction (stage **I**, Scheme 1). In the subsequent step in the mechanism, HL″ is eliminated. This electrocyclic reaction does not occur in the reaction of MeL with $[Ru(C_6H_6)Cl_2]_2$. Nevertheless the structure of the cation $[Ru(C_6H_6)(MeL)Cl]^+$ lends support to our proposition in Scheme 1 that in the reaction of $[Ru(C_6H_6)Cl_2]_2$ with HL, the ligand first binds ruthenium(II) in a bidentate fashion.



Scheme 1. A proposed mechanism for the reaction of $[Ru(C_6H_6)Cl_2]_2$ with HL. The H atoms of the pyridine rings and the coordinated benzene moieties are not shown.

To understand why in the reaction of RL with $[Ru(C_6H_6)Cl_2]_2$, electrocyclic reactions occur when R=H but not when R=Me, we have performed theoretical calculations by using the Gaussian 03 program.[23] The results are presented below.

Density functional calculations on the proposed electrocyclic reaction in free RL [Eq. (3)] were carried out at the B3LYP/6-31+G* level. For all the molecules appearing in Equation (3),

$$RL = L' + RL'' \tag{3}$$

with the obvious exception of L′, several different conformations were considered with various torsion angles around the rotatable bonds and these were geometry optimised to convergence. The $\Delta H°$ for the reaction in Equation (3) is found to be $-142.7\ kJ\,mol^{-1}$ for R=H and $-118.4\ kJ\,mol^{-1}$ for R=Me. Thus, at the B3LYP/6-31+G* level, the reaction in Equation (3) is more exothermic for R=H than for R=Me by $24.3\ kJ\,mol^{-1}$ in the gas phase. To find out to what extent the ruthenium-bound benzene moiety affects the $\Delta H°$ values, we have performed calculations on the reactions in Equations (4) and (5) by using density functional theory with the B3LYP functional.

$$[Ru(bz)(HL)Cl]^+ \rightarrow [Ru(bz)(L')Cl]^+ + HL'' \tag{4}$$

$$[Ru(bz)(MeL)Cl]^+ \rightarrow [Ru(bz)(L')Cl]^+ + MeL'' \tag{5}$$

The LANL2DZ basis set was used for Ru and 6-31+G* for other atoms. Starting models for $[Ru(C_6H_6)(MeL)Cl]^+$ and $[Ru(C_6H_6)(L')Cl]^+$ were taken from the crystal structures reported in this work. Although the structure of $[Ru(C_6H_6)(HL)Cl]^+$ shown in the reaction in Equation (4) has not been isolated, it seems most likely that the structure would be similar to that of $[Ru(C_6H_6)(MeL)Cl]^+$, and it was, therefore, generated from that structure by replacing the methyl groups by H atoms. These three Ru complexes were then geometry optimised to convergence as were HL″ and MeL″. Our calculations yielded similar $\Delta H°$ values of -124.2 and $-111.6\ kJ\,mol^{-1}$ for reactions in Equations (4) and (5). Examination of the structures showed that there was no steric crowding at any stage of Scheme 1 for either ligand.

Thus thermochemically, our electrocyclic reactions are equally feasible for both MeL and HL when coordinated to a metal. To understand the differential reactivities of HL and MeL, we have performed calculations on the transition states with model ligand systems RL‴ in the gas phase. RL‴ is a simplified version of RL in which the phenyl groups and an inactive pyridine moiety are omitted. The calculations have been carried out with and without complexation of the ligand to the $[RuCl(C_6H_6)]^+$ moiety to assess the importance of the presence of the metal. With metal complexation, the calculations have been carried out at the B3LYP/LANL2DZ level for Ru and B3LYP/6-31+G* for Cl, N, C and H, but in the absence of the metal at the B3LYP/6-31+G* level.

The results for the model metal complexes (Figures 3 and 4) are discussed first. The transition state Ru-H-**TS** (Figure 3) is encountered on going from stage **I** to stage **II** of Scheme 1 for HL‴. In the case of MeL‴, the transition

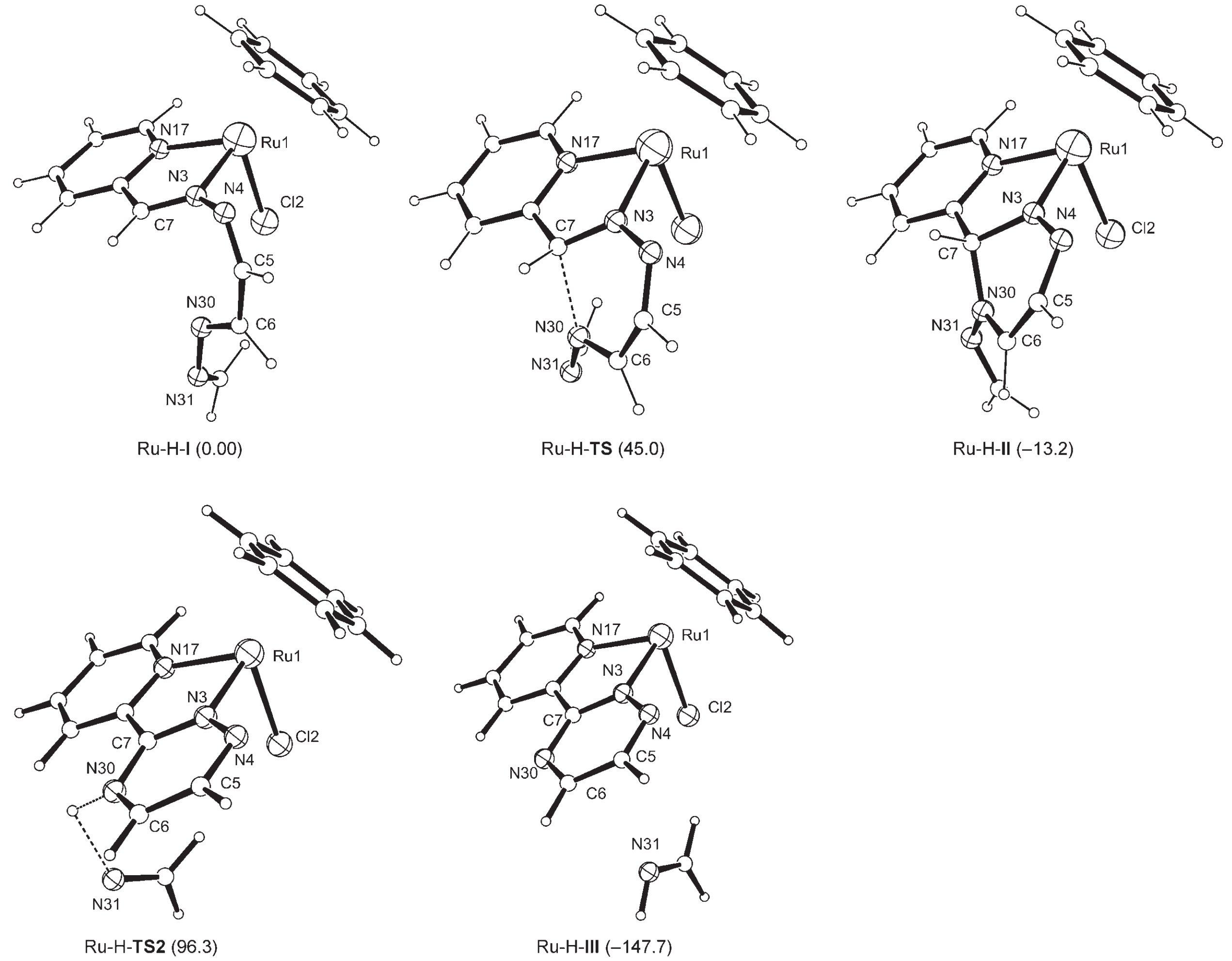
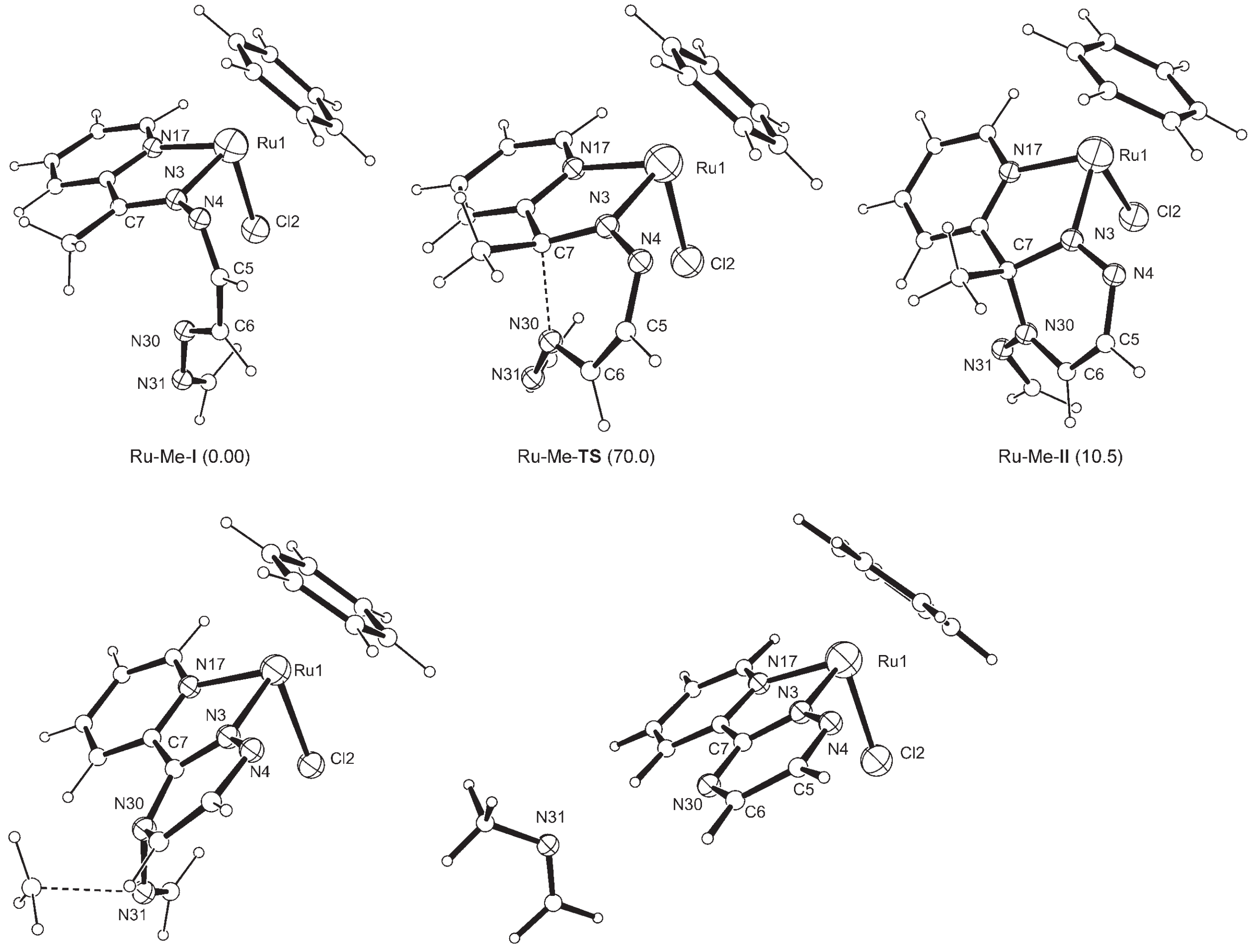


Figure 3. Calculated relative energies (shown in parentheses, kJ mol^{-1}) and optimised structures of the various species involved in the gas-phase transition-state calculations for HL′′′ given in Scheme 1. Ru-H-**I** represents stage **I**, Ru-H-**II** represents stage **II** and Ru-H-**III**, stage **III**. Ru-H-**TS** is the transition state between Ru-H-**I** and Ru-H-**II** and Ru-H-**TS2**, the transition state between Ru-H-**II** and Ru-H-**III**.

state for the same process is Ru-Me-**TS** (Figure 4). Ru-H-**TS** and Ru-Me-**TS** have been confirmed as being transition states by one negative frequency (−303.4 cm^{-1} for Ru-H-**TS** and −339.8 cm^{-1} for Ru-Me-**TS**). In the transition states, the C7−N30 distance is 1.968 Å in Ru-H-**TS** and 1.950 Å in Ru-Me-**TS**. The energy barriers for both reactions in Equations (4) and (5) are sufficiently low for both reactions to proceed at room temperature: 45.0 kJ mol^{-1} for R = H and 70.0 kJ mol^{-1} for R = Me.

We now consider the electrocyclic reactions in free RL′′′. Both ligands MeL′′′ and HL′′′ have four rotatable bonds, the Ph−C7, N3−N4, C5−C6 and N30−N31 bonds, respectively, and conformational analysis showed that the *trans*, *trans*, *trans*, *trans* (*tttt*) conformation had the lowest energy in both cases (Figure 5). This was established by calculations at the B3LYP/6-31+G* level on 2^4 conformations, with each torsion angle producing starting values of 0 or 180°. Indeed for both structures, this conformation was the lowest energy by approximately 21 kJ mol^{-1}. However, the difference in energy between *tttt* and *cttt* could not be accurately established, as for both molecules, the *cttt* conformation proved unstable and converged to the *tttt* conformation. Clearly the *cis* arrangement for N3 and N17 around the C7−Ph ring is unstable in the absence of the metal atom due to interactions between *ortho* hydrogen atoms. In these minimum energy *tttt* conformations, both ligands were planar with four 180° torsion angles, values which can be compared with the values of −2.8, 73.9, −20.4, −104.7° and −5.1, 85.9, −18.0, −104.3° found for the optimised starting geometries of the two ruthenium complexes shown in Figures 3 and 4. By using these minimum-energy conformations we were not able to locate transition states for the cyclisation reaction, which indicates that the reaction cannot proceed from the low energy *tttt* conformation of the ligands. What we did find, however, was that the low-energy starting conformations of both ligands are significantly more stable than the bicyclic products by 49.6 and 39.6 kJ mol^{-1}, respectively. It should be noted from Figures 3 and 4 that in the Ru-assisted processes for the model ligand systems, $\Delta H°$ is −13.2 kJ mol^{-1} for R = H and 10.5 kJ mol^{-1} for R = Me. This



Ru-Me-I (0.00) Ru-Me-**TS** (70.0) Ru-Me-II (10.5)

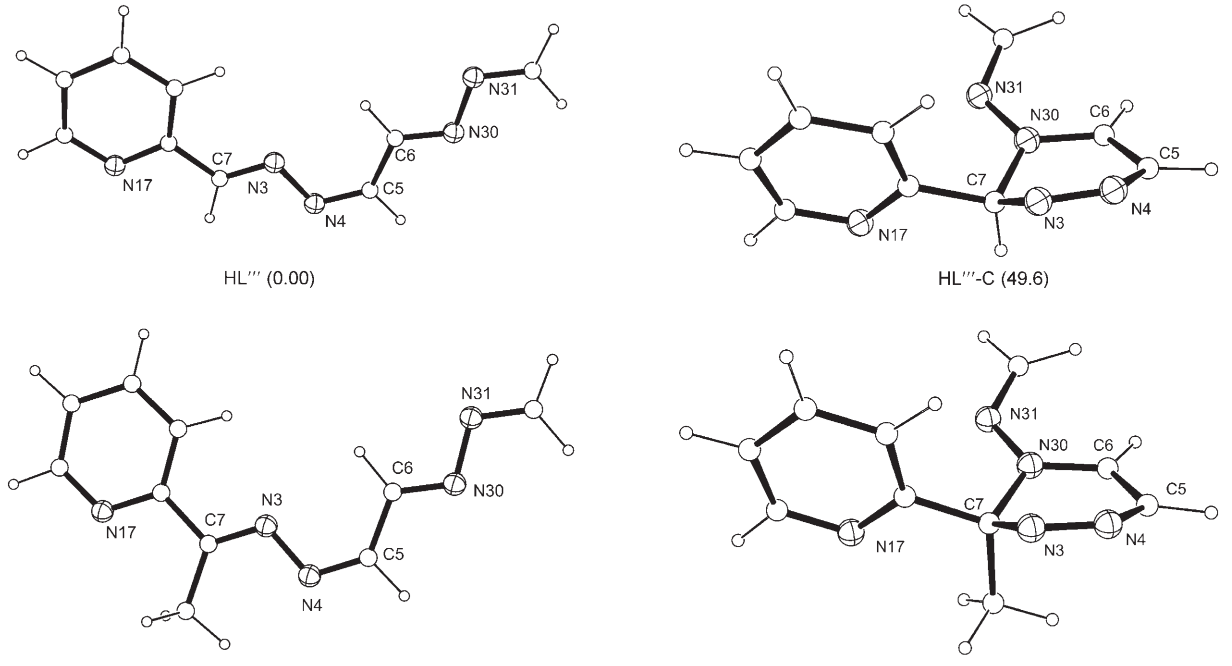
Ru-Me-**TS2** (329.1) Ru-Me-III (–120.8)

Figure 4. Calculated relative energies and optimised structures of the various species involved in the gas-phase transition-state calculations for MeL‴ given in Scheme 1. Ru-Me-**I** represents stage **I** , Ru-Me-**II** represents stage **II** and Ru-Me-**III**, stage **III**. Ru-Me-**TS** is the transition state between Ru-Me-**I** and Ru-Me-**II** and Ru-Me-**TS2**, the transition state between Ru-Me-**II** and Ru-Me-**III**.

emphasizes the importance of the formation of the Ru complex. Metal complexation facilitates the reaction by stabilising the *cis* conformation around the C7–Ph bond which is appropriate for cyclisation.

Previous theoretical work on cyclisation has included a study of the electrocyclisation of (*Z*)-hexa-1,3,5-triene and its heterosubstituted analogues.[19] Calculations were carried out with a variety of methodologies but we consider here results using B3LYP/6-31+G** which were similar to those obtained with much higher basis sets, such as QCISD(T) and MP4SDTQ, thus validating the method used in this current work. No metal complex was considered in that work. The relative energies for hexatriene and cyclohexadiene differed by $-51.1\,\mathrm{kJ\,mol^{-1}}$ at this level with a transition-state barrier of $126.0\,\mathrm{kJ\,mol^{-1}}$. When a terminal CH_2 group is replaced by N or O so that cyclisation produces dihydropyridine or 2H-pyran, then these numbers are significantly different at −29.2, 86.1 and 14.4, $90.0\,\mathrm{kJ\,mol^{-1}}$, respectively, values which are comparable with experiment. It was concluded that the lowering of the transition-state barrier by approximately $10\,\mathrm{kcal\,mol^{-1}}$ for the compounds containing terminal NH and O rather than CH_2 was due to the involvement of a lone pair on the heteroatom, which facilitates the interaction favouring the formation of the new bond, thus forming the six-membered ring. The relative energies of the acyclic and cyclic systems show that the electrocyclization is a highly exothermic process for hexatriene, much less so for pentadienimine and slightly endothermic for pentadienal. In our model complexes, the transition-state barriers are 45.0 and $70.0\,\mathrm{kJ\,mol^{-1}}$ for HL‴ and MeL‴, respectively. These values are somewhat less than those found for the parent simple rings.[20] A difference caused by metal complexation is that without the metal, the electrocyclic reactions in RL‴ are quite endothermic (R = H, $49.6\,\mathrm{kJ\,mol^{-1}}$; R = Me, $39.6\,\mathrm{kJ\,mol^{-1}}$) but with the metal, it is exothermic ($-13.2\,\mathrm{kJ\,mol^{-1}}$) for R = H and slightly endothermic ($10.5\,\mathrm{kJ\,mol^{-1}}$) for R = Me.

From the foregoing discussions, it is indicated that both reactions in Equations (4) and (5) are kinetically feasible as the energy barriers would not be significant. Still only the



HL‴ (0.00)

HL‴-C (49.6)

MeL‴ (0.00)

MeL‴-C (39.6)

Figure 5. Relative energy-optimised structures of the model acyclic ligands RL‴ and their electrocyclised products RL‴-C.

reaction in Equation (4) occurs under our experimental conditions and not the reaction in Equation (5). A close examination of Scheme 1 reveals that formation of $[\mathrm{Ru}(C_6H_6)(L')Cl]^+$ takes place by a double domino reaction—the first is the electrocyclic reaction in a C=N−N=C−C=N sequence, while the second one is an elimination reaction with the formation of metal-bound aromatic L′. We wish to point out here that electrocyclic reactions in a C=N−N=C−C=N system is unprecedented in the area of organic chemistry. As the electrocyclic reaction is reversible, the elimination of HL″ with the formation of L′ drives the complete equilibrium toward completion of the domino process. In the case of HL, a C−H bond is broken to result in the elimination of HL″. This means that for a similar domino reaction to occur in MeL, breaking of a C−C bond would be required to bring about the elimination of MeL′. But breaking of a C−C bond is much more difficult than breaking of a C−H bond. This accounts for the observed stability of $[\mathrm{Ru}(C_6H_6)(\mathrm{MeL})Cl]^+$. To test this hypothesis, we have performed theoretical calculations on the elimination step in our model complexes described above (see Figures 3 and 4).

In the model complexes, the elimination step involves breaking of the bond between the hydrogen atom in Ru-H-**II** (or the methyl group in Ru-Me-**II**) bonded to C7. It was considered likely that this step was accompanied by the breaking of the N30−N31 bond and the formation of a bond between the hydrogen atom (or methyl group) to N30. The results of our transition-state calculations for Ru−H are shown in Figure 3 and those for Ru−Me in Figure 4.

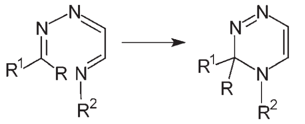
For Ru−H, the transition state has one negative frequency at $-703.19\,\mathrm{cm}^{-1}$. The structure of the transition state is somewhat surprising as the hydrogen has migrated from C7 to form a strong interaction with N30. The N30−H distance is 1.014 Å with N31−H 1.932 Å. However, an intrinsic reaction coordinate (IRC) calculation with Gaussian 03 by using this transition state clearly showed the increase of the N30−H distance and the formation of the N31−H bond as shown in Figure 3. The energy barrier for Ru-H-**TS2** is $96.3\,\mathrm{kJ\,mol^{-1}}$ and the relative energy of the final product Ru-H-**III** is $-147.7\,\mathrm{kJ\,mol^{-1}}$ relative to the starting reactant Ru-H-**I**.

However, the reaction with Ru−Me is somewhat different. The transition state Ru-Me-**TS2** shown in Figure 4 with a frequency of $-410.7\,\mathrm{cm}^{-1}$ does not show the methyl group attached to N30, indeed the C−N distance is 2.387 Å. Rather there is an interaction with N31 with a distance of 2.089 Å. IRC calculations show that this C−N31 bond is being formed and that the transition state leads to the product Ru-Me-**III** as shown in Figure 4. For Ru-Me-**TS2**, the energy barrier is much larger than in the case of Ru-H-**III** with a value of $329.1\,\mathrm{kJ\,mol^{-1}}$.

Thus the large difference in the activation energies involved in the elimination step in our model complexes indicate why the reaction is observed for Ru−H but not for Ru−Me. Consequently a C−H versus a C−C bond breaking controls the global domino reaction operative in our systems.

Conclusion

The usual electrocyclic reaction in a $R^1RC{=}N{-}N{=}C{-}C{=}NR^2$ system is shown in the reaction in Equation (6). However, in our metal-assisted cases, the reaction goes one step further to give a 6π-electron system with the elimination of $R{-}R^2$ [Eq. (7)]. Thus, we have a case of double domino electrocyclic/elimination reactions (Scheme 1). It is the ease of the breaking of the C–R bond in the elimination step which decides whether the metal-assisted double domino reaction will take place.



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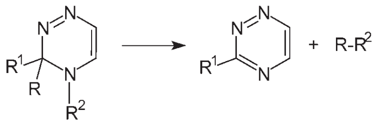

(7)

It should be noted that the elimination step in our domino reaction generates a new bidentate ligand L′ which is aromatic. This aromaticity may be demanded by the metal centre. However, not all metal ions can bring about the observed domino reaction. For example, reactions of RL with Cu^+ and Ag^+ yield metal complexes of unchanged RL.[15,24,25] All our attempts to generate L′ from HL and MeL thermally have not been successful. Thus, ruthenium(II) here plays a distinct role in bringing about the observed double domino reaction for HL.

Experimental Section

General: HL and MeL were synthesised as reported earlier.[16] $[Ru(C_6H_6)Cl_2]_2$ was prepared by a literature procedure.[26] Microanalyses were performed by a Perkin–Elmer 2400II elemental analyser. FTIR spectra (KBr) were recorded on a Nicolet Magna-IR spectrophotometer (Series II) and UV-visible spectra on a Shimadzu UV-160 A spectrophotometer. Molar conductance was measured by using a Systronics (India) Conductivity Meter 306.

Computations: Calculations on the ligands and metal complexes including the location of transition states were carried out with the B3LYP functional. The LANL2DZ basis set was used for Ru together with 6-31+G* for the lighter atoms in metal complexes and 6-31+G* for the ligands. All calculations were carried out with the Gaussian 03 program.[23] All structures reported here were geometry optimised to convergence by using the default tests. All structures reported as transition states showed one negative frequency.

Synthesis of $[Ru(C_6H_6)(L')Cl]PF_6$ ([1]PF$_6$): $[Ru(C_6H_6)Cl_2]_2$ (0.12 g, 0.25 mmol) was added to a solution of HL (0.21 g, 0.5 mmol) and NH_4PF_6 (0.09 g, 0.5 mmol) in methanol (15 mL), and the resulting mixture was refluxed for 2 h. The red reaction mixture was left in air for 4 h at room temperature and then a yellow-black precipitate was filtered off and dried in vacuo over fused $CaCl_2$. The product was recrystallised twice from dichloromethane as an orange-yellow compound. Yield: 0.06 g (18%); IR (KBr): $\tilde{\nu}=843$ (vs); 559 cm^{-1} (s) ($\nu(PF_6)$); Λ_M (MeCN): 135 $\Omega^{-1}\,cm^2\,mol^{-1}$ (1:1 electrolyte); UV/Vis (MeCN): λ_{max} (ε_{max}): 204 (3.9×10^4), 299 (2.3×10^4), 337 (1.3×10^4), 416 nm ($5.5\times10^3\,dm^3\,mol^{-1}\,cm^{-1}$); elemental analysis calcd for $C_{26}H_{20}N_4ClF_6PRu$ (669.73): C 46.59, H 3.01, N 8.36; found: C 46.57, H 3.26, N 8.26

Synthesis of $[Ru(C_6H_6)(MeL)Cl]PF_6\cdot4H_2O$ ([2]PF$_6\cdot4H_2O$): This compound was prepared by an analogous method to **1** by using $[Ru(C_6H_6)Cl_2]_2$ (0.12 g, 0.25 mmol), MeL (0.23 g, 0.5 mmol) and NH_4PF_6 (0.09 g, 0.5 mmol) and obtained as a yellow crystalline compound. Yield: 0.08 g (18%); IR (KBr): $\tilde{\nu}=840$ (vs); 558 cm^{-1} (s) ($\nu(PF_6)$); Λ_M (MeCN): 142 $\Omega^{-1}\,cm^2\,mol^{-1}$ (1:1 electrolyte); UV/Vis (MeCN): λ_{max} (ε_{max}): 201 (6.6×10^4); 290 ($3.7\times10^4\,dm^3\,mol^{-1}\,cm^{-1}$); elemental analysis calcd for $C_{34}H_{38}N_6ClF_6PO_4Ru$ (875.87): C 46.58, H 4.37, N 9.59; found: C 46.66, H 4.24, N 9.50.

X-ray crystallography: Data for [**1**]PF$_6$·1.5(acetone) and [**2**]PF$_6$·acetone were collected at 150 K on a Bruker SMART APEX CCD diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Data reduction was performed with SAINT+ and absorption corrections applied by using SADABS. The structures were solved by direct methods[27] and refined[28] on F^2 by using the SHELXTL PLUS V6.10 programme package. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically by using a riding model. Table 1 lists the crystallographic data for the two complexes. CCDC-263354 ([**1**]PF$_6$·1.5(acetone)) and -263355 ([**2**]PF$_6$·acetone) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for the complexes [**1**]PF$_6$·1.5(acetone) and [**2**]PF$_6$·acetone.

	[**1**]PF$_6$·1.5(acetone)	[**2**]PF$_6$·acetone
empirical formula	$C_{30.5}H_{29}ClF_6N_4O_{1.5}PRu$	$C_{37}H_{36}ClF_6N_6OPRu$
M_w	757.07	862.21
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a [Å]	11.2029(19)	15.1255(11)
b [Å]	11.0870(19)	16.0851(12)
c [Å]	26.329(5)	17.1245(12)
α [°]	90.00	114.7730(10)
β [°]	95.103(3)	92.1870(10)
γ [°]	90.00	102.2620(10)
V [Å^3]	3257.2(10)	3658.4(5)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.544	1.565
μ [mm^{-1}]	0.679	0.616
$F(000)$	1528	1752
Crystal size [mm]	0.34 × 0.30 × 0.18	0.45 × 0.38 × 0.22
θ range [°]	1.55–28.33	1.39–28.29
index ranges	−14/14, −14/14, −33/33	−19/20, −20/20, −22/22
no. of reflns		
unique	7778	16856
observed [$I>2\sigma(I)$]	6821	15417
parameters	424	991
R indices (observed data)	$R_1=0.0554$ $wR_2=0.1512$	$R_1=0.0411$ $wR_2=0.1007$
R indices (all data)	$R_1=0.0615$ $wR_2=0.1569$	$R_1=0.0451$ $wR_2=0.1036$
largest diff. peak/hole [e Å^{-3}]	2.201, −0.687	1.026, −0.735

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