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Conversion of hydrazides into *N,N'*-diacylhydrazines in the presence of ruthenium(II)-arene complex

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Abstract

Mono and dinuclear *p*-cymene-ruthenium(II) complexes [RuCl(**L**^{1})(η^6-*p*-cymene)]Cl, where **L**^{1} is propionic acid hydrazide (**1**) and [Ru_2Cl_2(**L**^{2})(η^6-*p*-cymene)$_2$], where **H$_2$L**^{2} is N^1,N^2-dipropionylhydrazine (**2**) were prepared by reaction of [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ with the corresponding ligand precursor. Upon the reaction of [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ with butyric acid hydrazide and pentanoic acid hydrazide in 1:1 molar ratio *in situ* formation of tetradentate bridging ligands, N^1,N^2-dibutanoylhydrazine and N^1,N^2-dipentanoylhydrazine, respectively, occurred and the dinuclear complexes [Ru_2Cl_2(**L**^{3})(η^6-*p*-cymene)$_2$] (**3**) and [Ru_2Cl_2(**L**^{4})(η^6-*p*-cymene)$_2$] (**4**) were isolated. The compounds were characterised by elemental analysis, ESI-mass spectrometry, IR, 1D and 2D NMR spectroscopies. Single crystals of [**3**][$RuCl_2(\eta^6$-*p*-cymene)]$_2$ were grown from a mixture of N^1,N^2-dibutanoylhydrazine and excess [$RuCl_2(\eta^6$-*p*-cymene)]$_2$. The structures of all complexes were established by single crystal X-ray crystallography. According to these data in both the mono- and dinuclear complexes the ruthenium atoms adopt the usual „three-leg piano-stool" geometry which is common for this type of complexes. Combining DFT calculations with the characterization of final products by X-ray single-crystal diffraction, possible reaction mechanism was discussed.

Introduction

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Dinuclear metal complexes, called also "clips" represent building blocks for the multifunctional supramolecular systems with diverse potential applications.[1,2,3] In recent years, dinuclear and polynuclear ruthenium complexes incorporating di- and tridentate bridging ligands have received considerable attention because of their possible applications in homogeneous catalysis, as multielectron storage systems[4] and as antitumour agents.[5] Through the choice of chelating bridging linkers and introduction of various functional groups the reactivity of the metal center can be tuned. Recent efforts have focused on attempts to optimise the biological properties of arene ruthenium-assemblies.[6] Of note is also the design and synthesis of new polynuclear ruthenium complexes with structural diversity.[7]

A large number of the reported complexes in the literature is formed by self-assembly reactions.[8]

The approach often includes *in situ* reactions of the starting building blocks in the presence of metal ions with formation of new organic product (ligand) isolated as a metal complex. An advantage of this approach is the one step reaction to metal complex which does not need the direct ligand synthesis followed by complex formation reaction. The main disadvantage is the difficulty in isolation of the organic product formed. One possibility is via demetallation, which, however, not always is easily accomplished, and is mainly developed for first-row transition metals. Depending on the nature of ligating atoms, both chelating and bridging ligands can be formed, leading to the compounds of varying nuclearities.[9]

We have been interested in the reactions of the chlorido bridged arene ruthenium complex $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with a variety of different ligand precursors.[10] A number of mononuclear arene-ruthenium(II) complexes with caprylic acid hydrazide (a hydrazide with a long hydrocarbon chain) and isonicotinic acid hydrazide (a hydrazide with an aromatic pyridine ring), have been reported.[11] X-ray structure analysis confirmed the coordination of caprylic acid hydrazide in a bidentate manner through the hydrazide moiety.

In order to examine the effect of the hydrocarbon chain length on both physicochemical and cytotoxic properties of *p*-cymene ruthenium complexes attempts to prepare new mononuclear complexes of aliphatic hydrazides were undertaken. While the reaction of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with propionic acid hydrazide afforded the expected product, with butyric acid hydrazide and pentanoic acid hydrazide dinuclear complexes with the bridging, *in situ* formed N^1,N^2-

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dibutanoylhydrazine and N^1,N^2-dipentanoylhydrazine were isolated. The dimeric complex with N^1,N^2-dibutanoylhydrazine was also obtained by the reaction of starting dinuclear complex with *a priori* prepared N^1,N^2-dibutanoylhydrazine. The corresponding dinuclear complex with N^1,N^2-dipropionylhydrazine was prepared by the reaction of starting complex with *a priori* synthesised N^1,N^2-dipropionylhydrazine.

Transformation of hydrazides into *N,N'*-diacylhydrazines is a well-known reaction in organic chemistry and usually demands oxidation agents like oxone,[12] selenium based compounds,[13] iodine,[14] iodobenzene diacetate,[15] sodium perborate,[16] or mercury(II) acetate.[17] Microwave irradiation is also efficient.[18] Depending on the nucleophile present in reaction mixture, hydrazide can be transformed into aldehyde, carboxylic acid or ester.[19] This kind of transformations is also performed in the presence of thallium,[20] or transition metal ions, e.g, lead,[21] copper,[22] iron[23] or manganese.[24] In the present study this transformation occurred in the presence of ruthenium arene complex. The reaction is presumably facilitated by the coordination of butyric - or pentanoic acid hydrazide to ruthenium centre.

All new complexes were characterised by elemental analysis, ^{1}H and ^{13}C NMR, UV–vis and ESI-mass spectrometry, as well as by single crystal X-ray crystallography. On the basis of spectroscopic characterization and DFT calculations, a mechanism of *in situ* transformation was proposed.

Results and discussion

Synthesis of the ligand precursors and ruthenium(II)-arene complexes

Disubstituted acyl hydrazines $\mathbf{H_2L^2}$ and $\mathbf{H_2L^3}$ were obtained by condensation of hydrazides with the corresponding acyl chlorides, in the presence of potassium carbonate in water as shown in Scheme 1. The products precipitated directly from the reaction mixture or after evaporating the solvent under reduced pressure.

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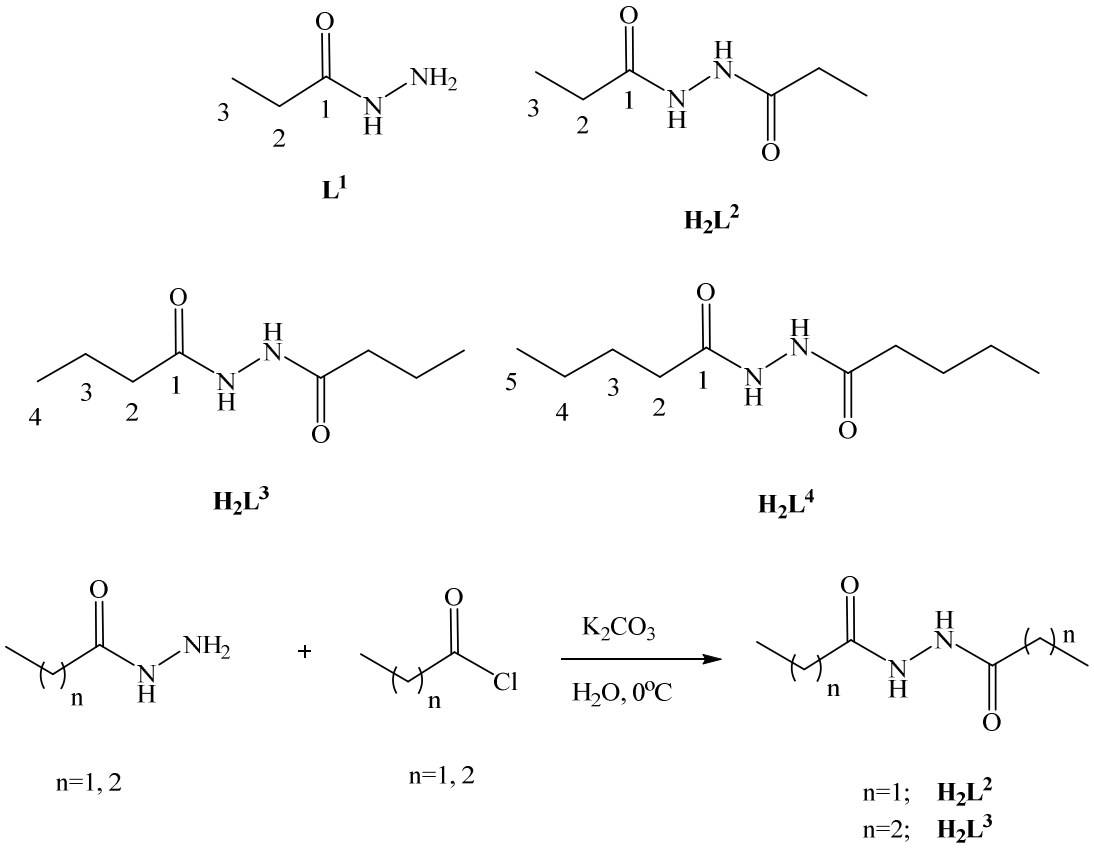

Scheme 1

Surprisingly, the reaction of butyric acid hydrazide and pentanoic acid hydrazide with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ afforded *N,N′*diacylhydrazines $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ isolated as dinuclear ruthenium(II) complexes **3** and **4**, respectively. Unlike, in the case of the propionic acid hydrazide, formation of N^1,N^2-dipropionylhydrazine $\mathbf{H_2L^2}$ as ruthenium(II)-arene complex was not observed. Instead, complex **1** (Scheme 2) was isolated. However, dinuclear species **2** was obtained from *a priori* synthesised $\mathbf{H_2L^2}$ and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ in 1:1 molar ratio. The complex **3** prepared from $\mathbf{H_2L^3}$ and ruthenium(II)-*p*-cymene dimer was identical to that prepared from butyric acid hydrazide and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$.

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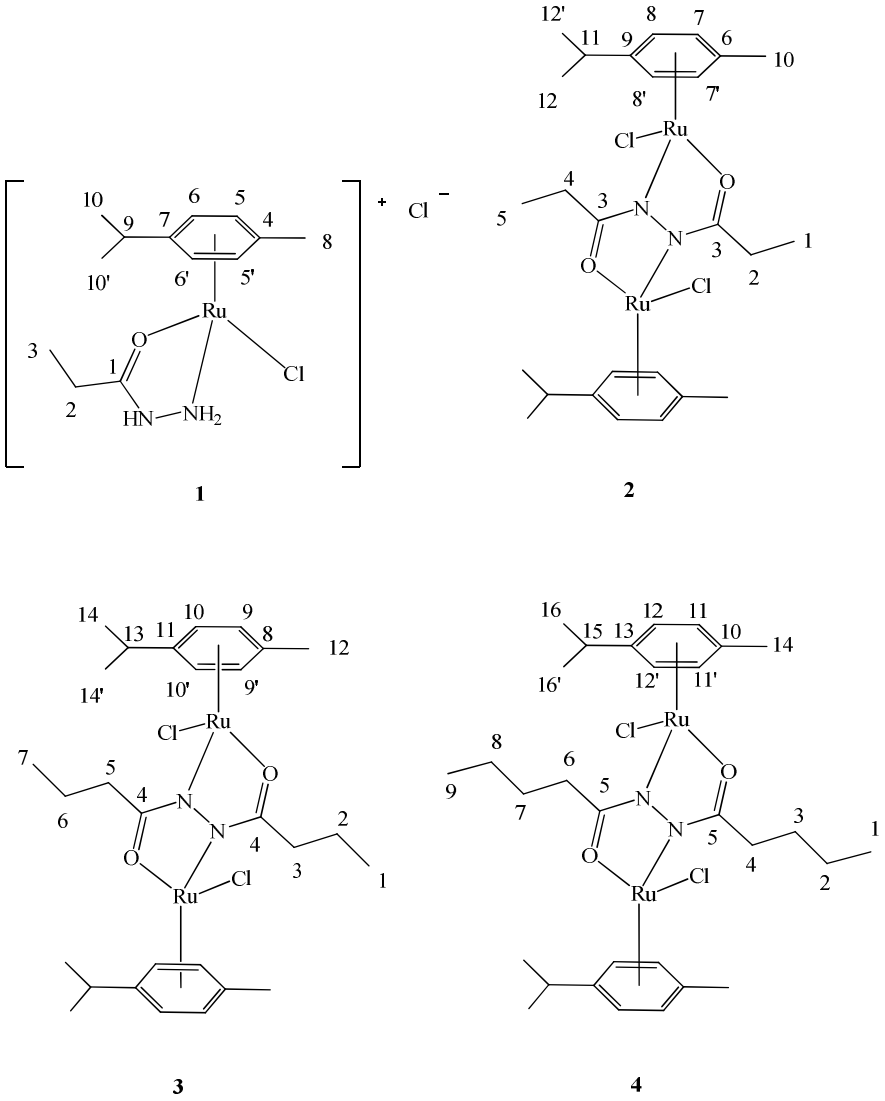

Scheme 2

Spectroscopy

The infrared spectra of the ligand precursors and the corresponding Ru(II) complexes were compared in order to gain preliminary information about the coordination mode of the ligands to the metal centre. The major changes are noticed in N-H stretching region of asymmetric and symmetric vibrations in the spectra of *N,N'*-diacylhydrazines $\mathbf{H_2L^{2\text{-}4}}$ and those of **2-4.** Spectra of $\mathbf{H_2L^{2\text{-}4}}$ contain a strong sharp band at 3200 cm^{-1} and this band is missing in the spectra of **2-4**. The C=O vibrations in IR spectra of $\mathbf{H_2L^{2\text{-}4}}$ are in the range 1585-1598 cm^{-1}, while those of the corresponding

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complexes **2-4** are shifted markedly (1528-1539 cm^{-1}). Similar observations are of note for $\mathbf{L^1}$ and **1**. These data suggest coordination of $\mathbf{L^1}$-$\mathbf{L^4}$ to ruthenium(II) via both carbonyl group and nitrogen atom.

The ^{1}H NMR spectra of the complexes show a characteristic pattern originating from the *p*-cymene moiety. In the spectra of complexes **2-4** proton signals from the aromatic ring are separated in two groups, one at around 5.35 ppm corresponding to three protons and another at around 5.00 ppm corresponding to one proton. A different pattern is observed in spectrum of **1**, where signals at 5.97 ppm correspond to two protons and resonances at 5.78 and 5.72 ppm to the other two protons. Isopropyl group from *p*-cymene shows a characteristic pattern for this type of ruthenium complexes.

In the spectrum of **1**, signals for methylene group of $\mathbf{L^1}$ are split into two multiplets at 2.49 and 2.26 ppm. The methyl group from the ligand appears at 1.15 ppm. In the spectra of **2** and **3** signals of aliphatic protons of ligands have different shifts compared to these of the free proligand. $\mathbf{H_2L^2}$ has two signals (CH_2 and CH_3 proton signals) and $\mathbf{H_2L^3}$ has three (two CH_2 and CH_3 proton resonances), as expected. Upon coordination to ruthenium centre, all signals from the ligands are well-separated. In spectrum of **2** terminal methyl protons resonate at 1.28 and 1.24 ppm. One CH_2 group is split into two multiplets at 2.90 and 2.69 ppm. Another CH_2 group appears at 3.71 ppm as a quartet. These resonances were also assigned by COSY and HSQC NMR measurements. In the spectrum of **3** the first two CH_2 groups are split into two multiplets at 2.82 and 2.66 ppm, whereas further CH_2 groups are centred at around 1.81 ppm as a multiplet, and both terminal methyl groups are seen at 1.01 ppm as a triplet. The spectrum of **4** shows a triplet at 0.97 ppm from terminal methyl groups, multiplets at 1.39, 1.77 and 2.70 ppm from three (distant and nearest) CH_2 groups. The reason why distant CH_2 groups are at the same place may be in the length of aliphatic chain of the ligand and consequently the fact that the coordination has little effect on remote protons.

The ^{13}C NMR spectra of **2 - 4** are also in agreement with proposed structures. Resonances in the δ range 78.84–101.84 ppm belong to aromatic carbons. Methine carbon of isopropyl group is found at around 30 ppm and its methyl groups carbons at around 22 ppm, while methyl group carbon in *para* position to isopropyl group is seen at around 18 ppm. Carbons from the ligand in **1** are at 173.75 (carbonyl group), 24.36 (CH_2 group) and 9.47 ppm (CH_3 group). In **2** carbon of carbonyl group is located at 174.38 ppm, carbon from CH_2 groups are at 58.14 ppm and 27.35 ppm, and methyl carbons are found at 18.29 and 11.74 ppm. The ^{13}C NMR spectrum of **3** provides

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resonances for carbons of the ligand at 173.75 ppm for carbonyl group, at 36.31 ppm resonates the carbon from nearest CH_2 group, at 20.70 ppm the carbon from more distant CH_2 group and terminal methyl groups are seen in ^{13}C NMR spectrum at 14.39 ppm. Complex **4** shows a signal at 173.88 ppm (C=O), at 34.06 from closer CH_2 group, at 29.65, 29.29, 22.52 and 22.12 ppm from remote CH_2 group and methyl carbon at 14.03 ppm.

The ESI mass spectrum of **1** recorded in the positive ion mode showed a peak with *m/z* 359.04 attributed to the $[M\text{-}Cl]^+$. Complexes **2-4** exhibit peaks attributed to the $[M\text{-}Cl]^+$ at *m/z* 649.21, 677.08 and 704.13, respectively.

X-ray crystallography

The results of X-ray diffraction studies of **1**, **2**·2EtOH, **[3][RuCl$_2$(η^6-*p*-cymene)]$_2$** and **4** are shown in **Figures 1–4**. Each ruthenium atom has the typical "three leg piano-stool'' geometry, which is common for a large number of ruthenium(II) arene species. Despite the presence of one stereogenic centre in **1** or two stereogenic centres in **2 - 4**, the complexes are not chiral and crystallise in centrosymmetric space groups $P2_1/c$, and P-1, respectively.

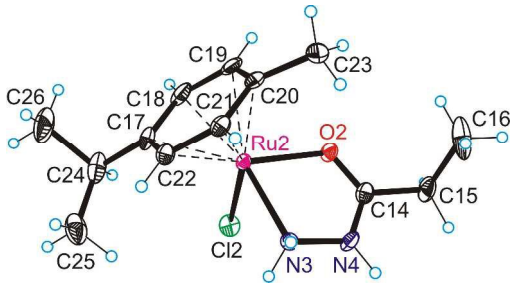

Figure 1. ORTEP view of one of the two crystallographically independent cations $[RuCl(L^1)(\eta^6\text{-}p\text{-cymene})]^+$ in **1** with thermal ellipsoids at 50% probability level. Selected bond distances (Å) and angles (deg): Ru2–O2 = 2.0880(17), Ru2–N3 = 2.115(2), Ru2–Cl2 = 2.4028(7), Ru2–C17 = 2.198(3), Ru2–C18 = 2.176(3), Ru2–C19 = 2.159(3), Ru2–C20 = 2.166(3), Ru2–C21 = 2.145(3), Ru2–C22 = 2.171(3), N3–N4 1.423(3), C14–O2 1.250(3), O2–Ru2–N3 77.63(7).

The N–N bond lengths in all three complexes correspond to typical single bonds. The C–O bond length in **1** has predominantly a double bond character, while in **2-4** the electronic delocalisation is slightly more pronounced leading to elongation of these by ca. 0.04 Å. The bond

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lengths around ruthenium(II) are well-comparable to those in other related mono- and dinuclear *p*-cymene ruthenium complexes.[22]

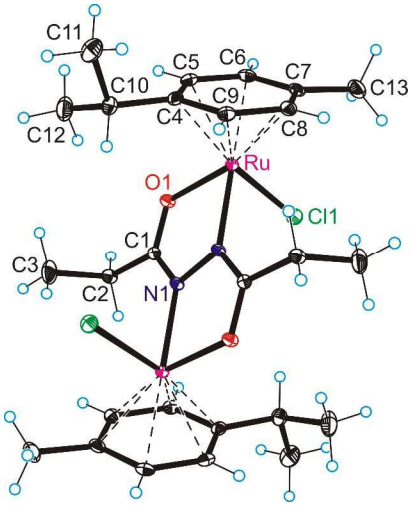

Figure 2. ORTEP view of **2** with thermal ellipsoids at 50% probability level. Selected bond distances (Å) and angles (deg): Ru–O1 = 2.0534(7), Ru–N1^{i} = 2.0994(8), Ru–Cl1 = 2.4290(3), Ru–C4 = 2.1841(10), Ru–C5 = 2.1674(10), Ru–C6 = 2.2010(10), Ru–C7 = 2.2164(10), Ru–C8 = 2.2024(10), Ru–C9 = 2.1466(10), N1–N1^{i} = 1.4345(16), C1–O1 = 1.2934(12), O1–Ru–N1^{i} 76.03(3).

The Ru···Ru distances in **2** and **3** are of 4.9498(2) and 4.9356(3) Å. These are well-comparable to that of 4.9411(5) Å in a related dinuclear *p*-cymene ruthenium complex with diethyl-1,2-diazenedicarboxylate.[11]

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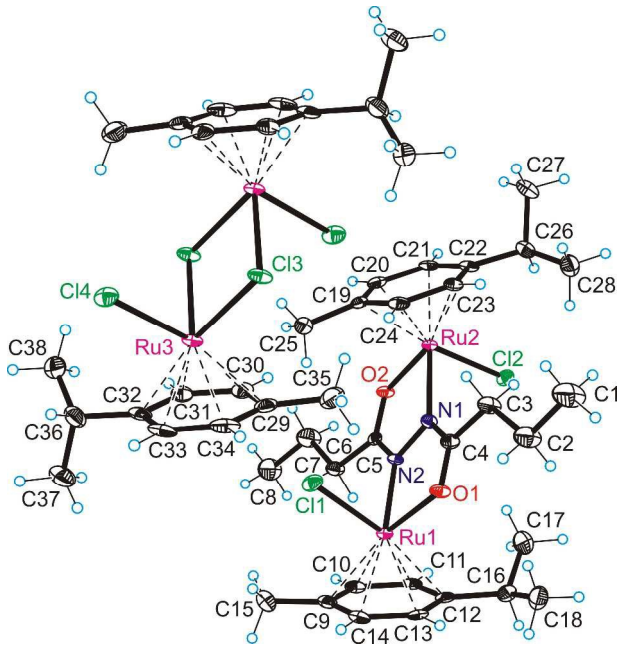

Figure 3. ORTEP view of **[3][RuCl$_2$(η^6-*p*-cymene)]$_2$** with thermal ellipsoids at 50% probability level. Selected bond distances (Å) and angles (deg): Ru1–O1 = 2.0678(15), Ru–N2 = 2.1006(17), Ru1–Cl1 = 2.4176(6), Ru1–C9 = 2.208(2), Ru1–C10 = 2.197(2), Ru1–C11 = 2.172(2), Ru1–C12 = 2.201(2), Ru1–C13 = 2.187(2), Ru1–C14 = 2.201(2), O1–Ru1–N2 76.12(6); Ru2–O2 = 2.0639(15), Ru2–N1 = 2.0949(18), Ru2–Cl2 = 2.4102(6), Ru2–C19 = 2.172(2), Ru2–C20 = 2.158(2), Ru2–C21 = 2.191(2), Ru2–C22 = 2.222(2), Ru2–C23 = 2.202(2), Ru2–C24 = 2.151(2), N1–N2 = 1.433(3), C4–O1 = 1.287(3), C5–O2 = 1.289(3), O2–Ru2–N1 76.11(6); Ru3–Cl3 = 2.4423(6), Ru3–Cl3^{i} = 2.4424(5), Ru3–Cl4 = 2.4087(6), Ru3–C29 = 2.205(2), Ru3–C30 = 2.178(2), Ru3–C31 = 2.145(2), Ru3–C32 = 2.168(2), Ru3–C33 = 2.148(2), Ru3–C34 = 2.158(2).

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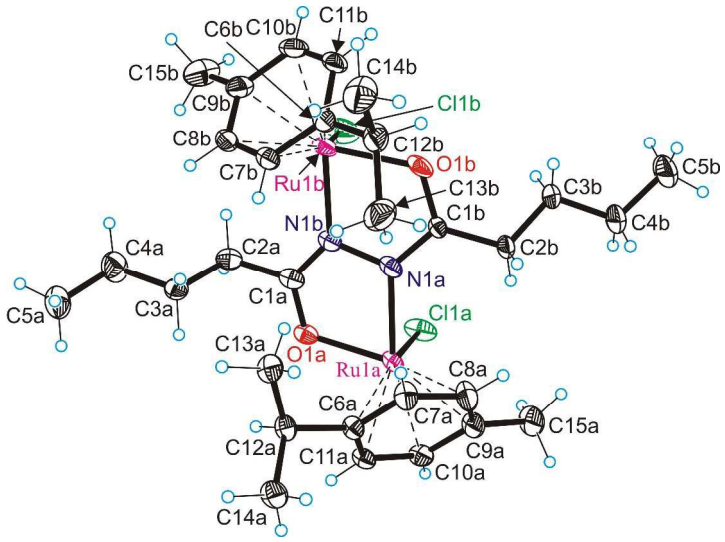

Figure 4. ORTEP view of **4** with thermal ellipsoids at 50% probability level. Selected bond distances (Å) and angles (deg): Ru1a–O1a = 2.0619(18), Ru1a–N1a = 2.091(2), Ru1a–Cl1a = 2.4135(7), Ru1a–C6a = 2.171(2), Ru1a–C7a = 2.147(3), Ru1a–C8a = 2.188(3), Ru1a–C9a = 2.216(3), Ru1a–C10a = 2.187(2), Ru1a–C11a = 2.185(2), O1a–Ru1a–N1a 76.04(8); Ru1b–O1b = 2.065(2), Ru1b–N1b = 2.087(2), Ru1b–Cl1b = 2.4244(8), Ru1b–C6b = 2.180(3), Ru1b–C7b = 2.175(2), Ru1b–C8b = 2.188(2), Ru1b–C9b = 2.204(3), Ru1b–C10b = 2.186(3), Ru1b–C11b = 2.187(3), N1a–N1b = 1.428(3), C1a–O1a = 1.292(3), C1b–O1b = 1.349(9), O1b–Ru1b–N1b 76.17(8).

It is apparent from the crystal structures (*vide infra*) that the formation of $\mathbf{H_2L^2}$ and $\mathbf{H_2L^3}$ takes place via the nucleophilic attack of the NH_2 group of the neighboring molecule of hydrazide on coordinated C=O group of hydrazide, followed by release of N_2H_4 and formation of *N,N′* diacylhydrazine bound to two ruthenium(II) centres with formation of the dinuclear complexes **3** and **4**.

It is well established that transition metals increase the polarity of C=O bonds upon coordination and in such a way facilitate the subsequent reactions like hydrolysis, esterification or transamination.[25] The IR stretching vibrations and ^{13}C NMR signal of C=O group are shifted to lower wavenumbers and higher chemical shifts in comparison to proligand, indicating the

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polarisation of C=O bond making it more reactive for nucleophilic attack of amine nitrogen of neighbouring hydrazide molecule.

A certain view on the possible reaction pathway (Scheme 3) can be deduced from the quantum chemical calculations which were performed for the reaction of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ complex (**R1**) with the butyric acid hydrazide (**R2**). If we suppose that the initial reaction step starts with the coordination of **R2** molecule to the metal atom, the energetically preferred intermediate **Ia** has only one Ru···Cl···Ru bridge stabilising the bis-arene complex and it exhibits one bond between the C=O group and Ru atom at 2.207 Å. The second direct addition of reactant molecule (**R2´**) to the **Ia** seems to be less preferable due to the steric reasons. The better steric conditions and the structural stability of reaction complex presumably ensure the consecutive elimination of two HCl molecules as shown in Scheme 3. The formed intermediate **IIIa** is stabilised *via* two bonds occurring between the N1 atom and both ruthenium atoms. The corresponding bond lengths are of 1.943 Å for N1–Ru and 2.133 Å for N1–Ru´. The bond length C=O–Ru is shortened (2.087 Å) compared to that in **Ia**. The second addition of **R2´** molecule results in the intermediate **IVa**, where a new bond C´=O´–Ru´ is formed. The two bond lengths Ru–O and Ru´···O´are of 2.086 and 2.082 Å, respectively. The hydrogen transfer from the hydrazine moiety to the neighbouring one in **IVa** leads to a stable intermediate **Va**. Finally, the abstraction of hydrazine molecule terminates the reaction and the final product **P** is generated. A view of the B3LYP optimal structures of all identified intermediates and their electronic energies are presented in **Fig. S15**. It should be also noted that calculated bond distances and angles in the DFT optimized structure satisfactorily agree with those from X-ray diffraction of **3** within ± 0,034 Å (see Table S1).

From the thermodynamic point of view, the Gibbs free energy ($\Delta_r G$) of the reaction can be calculated as the difference of Gibbs free energies of products and reactants

$$\Delta_r G = G(\mathrm{P}) + 2 \times G(\mathrm{HCl}) + G(\mathrm{N_2H_2}) - G(\mathrm{R1}) - 2 \times G(\mathrm{R2}) \quad (1)$$

The B3LYP energy for the gas-phase is 102 $kJ \cdot mol^{-1}$ what indicates the endothermic character of the studied reaction. This resulting energy is obtained as the sum of the reaction Gibbs free energies connected with the proposed individual reaction steps (see Scheme 3). The strongest endothermic character has the addition of **R2´** molecule to the **IIIa** intermediate. On the other hand, the final dichlorido-bridged product formation after hydrazine elimination from the intermediate **V** is strongly exothermic. Nevertheless, it should be noted that the heat of solvation of hydrogen chloride

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and hydrazine molecule in real environment will affect the final energy balance of chemical reaction.

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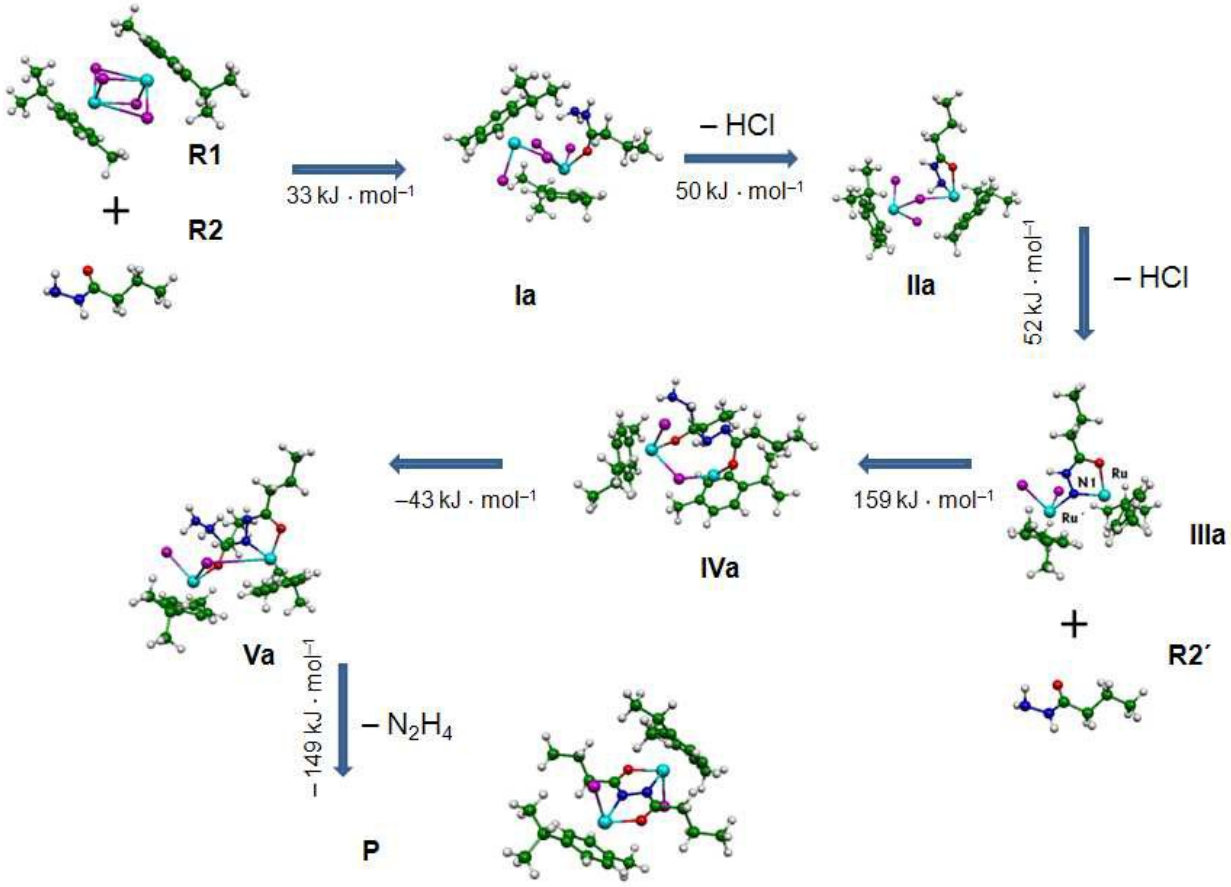
A tentative mechanism is purposed shown in Scheme 3.



Scheme 3. The proposed reaction pathway, the B3LYP optimal geometries of predicted intermediates and the Gibbs free energies of individual reaction steps; cyan spheres indicate ruthenium atoms, violet – chloride, blue – nitrogen, red – oxygen, green – carbon.

Experimental

Material and methods

$RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey (London, United Kingdom). $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ was prepared according to a published procedure.[26]

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Propionyl and butyryl chloride were purchased from Acros, butyric acid hydrazide and pentanoic acid hydrazide from Alfa Aesar, and propionic acid hydrazide from Sigma Aldrich. Solvents of *p.a.* quality were from Acros or Sigma Aldrich, and were used without additional purification. Elemental analysis was carried out with Elemental Vario EL III microanalyser. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer using ATR or KBr pellet technique. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer (at 200 and 50 MHz, respectively) and on a Bruker Ultrashield Advance III spectrometer (at 500 and 125 MHz, respectively) employing indicated solvents (vide infra) using TMS as the internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants J in Hz.

ESI mass spectra of ligand precursors and ruthenium complexes were recorded on 6210 Time-of-Flight LC-MS instrument (G1969A, Agilent Technologies) in positive ion mode and on Bruker Daltonics HCT 6000 mass spectrometer in positive ion mode by using as solvents CH_3CN/H_2O or CH_3CN.

Synthesis of ligand precursors

N^1,N^2-dipropionylhydrazine **H_2L^2**. Propionyl chloride (840 mg, 793 µl, 9.08 mmol) was added dropwise over 30 min to a stirred solution of propionic acid hydrazide (200 mg, 2.27 mmol) and potassium carbonate (627 mg, 4.54 mmol) in water (4 ml) at 0 °C. The mixture was stirred at 0°C for 2 h and at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica by using DCM/MeOH (1/4) as eluent. Yield: 190 mg (58%). IR (ATR): 3215 (s), 3046 (w), 2974 (m), 2938 (m), 1598 (s), 1489 (s), 1218 (m), 1073 (w), 883 (w), 654 (m). ^{1}H NMR (500 MHz, DMSO) δ_H 9.64 (NH, s, 1H), 2.14 – 2.08 (**H2**, q, J = 7.5 Hz, 2H), 1.03 – 0.97 (**H3**, t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ_C 171.89 (C1), 26.38 (C2), 9.67 (C3). (+)ESI-MS (m/z): $[M+Na]^+$ 167.14.

N^1,N^2-dibutanoylhydrazine **H_2L^3**. *n*-Butyryl chloride (1.03 g, 9.67 mmol) was added dropwise over 30 min to a stirred mixture of butyric acid hydrazide (290 mg, 2.84 mmol) and potassium carbonate (782 mg, 5.68 mmol) in water (3 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. The product was filtered off, recrystallised from ethanol (3 ml) and dried in air. Yield: 112 mg (23%). Anal. calcd for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.65; H, 9.38; N, 16.33. IR (ATR): 3206 (s), 3055 (w), 2964 (s), 2933 (m), 2870 (w), 1591 (s), 1503 (s), 1483 (s), 1437 (m),

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1201 (m), 1093 (w), 663 (m), 607 (w). ^{1}H NMR (500 MHz, DMSO-d6) δ_H 9.62 (s, 1H), 2.07 (**H2**, t, J = 7 Hz, 2H), 1.57 – 1.48 (**H3**, m, 2H), 0.87 (**H4**, t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 171.00 (C1), 35.09 (C2), 18.50 (C3), 13.52 (C4). (+)ESI-MS (m/z): $[M+Na]^+$ 195.12; $[2M+Na]^+$ 367.26.

Synthesis of ruthenium(II) complexes

[RuCl(propionylhydrazine)(η^6-*p*-cymene)]Cl (**1**). To a warm suspension of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (49.9 mg, 0.081 mmol) in isopropanol (7 ml) was added dropwise a suspension of propionic acid hydrazide (16.3 mg, 0.16 mmol) in isopropanol (3 ml). The mixture was stirred at room temperature for 3 h and allowed to stand in the fridge for 10 days. The product was filtered off, washed with isopropanol, diethyl ether and dried in vacuo. Yield: 34 mg (59%). Anal. calcd for $C_{13}H_{22}Cl_2N_2ORu$: C, 39.60; H, 5.62; N, 7.10. Found: C, 39.92; H, 5.36; N, 7.00. IR (ATR): 3211 (m), 3107 (m), 3052 (s), 2981 (s), 2958 (s), 2873 (s), 2775 (s), 2737 (s), 2654 (m), 1639 (s), 1569 (s), 1467 (m), 1381 (w), 1330 (w), 1291 (m), 1233 (s), 1090 (w), 885 (w), 785 (w), 551 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.08 (NH, s, 1H), 10.76 (NH from NH_2, d, J = 8.5 Hz, 1H), 6.47 (NH from NH_2, d, J = 8.5 Hz, 1H), 5.98 (**H5**, d, J = 6.0 Hz, 2H), 5.95 (**H6**, d, J = 5.5 Hz, 1H) 5.79 (**H5'**, d, J = 6.0 Hz, 1H), 5.73 (**H6'**, d, J = 6.0 Hz, 1H), 2.90 (**H9**, hept, J = 7.0 Hz, 1H), 2.54 – 2.46 (**H2**, hept, J = 7.5 Hz 1H), 2.45 – 2.36 (**H2**, hept, J = 8.0 Hz 1H), 2.26 (**H8**, s, 3H), 1.33 (**H10**, d, J = 7.0 Hz, 3H), 1.30 (**H10'**, d, J = 7.0 Hz, 3H), 1.15 (**H3**, t, J = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 181.33 (C1), 102.18 (C7), 95.98 (C4), 83.11 (C5), 82.97 (C5'), 79.93 (C6), 79.58 (C6'), 31.01 (C9), 24.63 (C2), 22.65 (C10), 22.23 (C10'), 18.36 (C8), 9.47 (C3). (+)ESI-MS (m/z): ($[M-Cl]^+$) 359.04.

[Ru_2Cl_2(N^1,N^2-dipropionylhydrazine)(η^6-*p*-cymene)$_2$] (**2**). To $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (62 mg, 0.101 mmol) in DCM (4 ml) was added N^1,N^2-dipropionylhydrazine (18 mg, 0.125 mmol) in ethanol (4 ml). The orange solution was stirred at room temperature for 4 h. Next day, the solution was concentrated, the product was filtered off, washed with Et_2O and dried. Yield: 46 mg (66%). A single crystal suitable for X-ray diffraction analysis was obtained by slow evaporation of the mother liquor. Anal. calcd for $C_{26}H_{38}Cl_2N_2O_2Ru_2$: C, 45.68; H, 5.60; N, 4.10. Found: C, 45.59; H, 5.57; N, 4.02. IR (ATR): 3391 (m), 3209 (m), 3055 (s), 3031 (s), 2965 (s), 2875 (s), 2781 (m), 1697 (m),

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1639 (s), 1570 (m), 1539 (s), 1464 (s), 1396 (s), 1234 (m), 1088 (w), 880 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.35 (**H7**, **7'**, **8'**, dt, J_1 = 16.5, J_2 = 6.0 Hz, 3H), 4.99 (**H8**, d, J = 5.5 Hz, 1H), 3.71 (**H4**, q, J = 7.0 Hz, 2H), 2.90 (**H2**, m, 1H), 2.74 – 2.65 (**H2**, **H11**, m, 2H), 2.20 (**H10**, s, 3H), 1.28 (**H1**, t, J = 7.5 Hz, 3H), 1.24 (**H5**, t, J = 7.0 Hz, 3H), 1.16 (**H12**, **12'**, dd, J_1 = 14.0, J_2 = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 174.38 (C3), 101.19 (C9), 98.49 (C6), 83.34 (C7), 80.49 (C8), 80.42 (C7'), 79.98 (C8'), 58.14 (C4), 30.43 (C11), 27.35 (C2), 22.40 (C12), 22.08 (C12'), 18.51 (C10), 18.29 (C5), 11.74 (C1). (+)ESI-MS (m/z): ($[M\text{-}Cl]^+$) 649.21.

[Ru_2Cl_2(N^1,N^2-dibutanoylhydrazine)(η^6-*p*-cymene)$_2$] (**3**) – Direct reaction. To a suspension of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (51 mg, 0.083 mmol) in ethanol (8 ml) was added a suspension of N^1,N^2-dibutanoylhydrazine (14 mg, 0.083 mmol) in ethanol (3 ml) at room temperature. The mixture was stirred at room temperature for 6 h and allowed to stand in the fridge for 7 days. The product was filtered off, washed with EtOH, diethyl ether and dried in vacuo. Yield: 35 mg (59%). Anal. calcd for $C_{28}H_{42}Cl_2N_2O_2Ru_2$: C, 47.25; H, 5.95; N, 3.94. Found: C, 47.50; H, 7.61; N, 3.56. IR (ATR): 3554 (m), 3495 (m), 3449 (s), 3032 (s), 2961 (s), 2928 (s), 2871 (s), 1529 (s), 1466 (m), 1390 (s), 1094 (w), 1041 (m), 880 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.37 – 5.29 (**H9, 9', 10'**, m, 3H), 4.99 (**H10**, d, J = 5.5 Hz, 1H), 2.83 (**H3** and **H5**, m, 1H), 2.74 – 2.61 (**H3** and **H5**, **H13**, m, 2H), 2.19 (**H12**, s, 3H), 1.88 – 1.74 (**H2** and **H6**, m, 2H), 1.17 (**H14**, **H14'**, dd, J = 14.5, 7.0 Hz, 6H), 1.01 (**H1** and **H7**, t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.75 (C4), 101.85 (C11), 98.10 (C8), 83.10 (C9), 80.96 (C9'), 80.73 (C10'), 79.84 (C10), 36.31 (C3, C5), 30.61 (C13), 22.62 (C14), 22.11 (C14'), 20.70 (C12), 18.59 (C2, C6), 14.39 (C1, C7). (+)ESI-MS (m/z): ($[M\text{-}Cl]^+$) 677.08; ($[M\text{-}2Cl]^{2+}$) 321.06.

[Ru_2Cl_2(N^1,N^2-dibutanoylhydrazine)(η^6-*p*-cymene)$_2$] (**3**) – *In situ* formation of ligand. To a solution of butyric acid hydrazide (33 mg, 0.32 mmol) in ethanol (3 ml) was added a warmed solution of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (100 mg, 0.16 mmol) in ethanol (8 ml). The mixture was stirred at room temperature for 16 h and allowed to stand in the fridge for 4 days. The product was filtered off, washed with cold ethanol, diethyl ether and dried in vacuo. Yield: 25.6 mg (44%). Anal. calcd for $C_{28}H_{42}Cl_2N_2O_2Ru_2$: C, 47.25; H, 5.95; N, 3.94. Found: C, 47.50; H, 7.61; N, 3.56. IR (ATR): 3554 (m), 3495 (m), 3449 (s), 3032 (s), 2961 (s), 2928 (s), 2871 (s), 1529 (s), 1466 (m), 1390 (s), 1094 (w), 1041 (m), 880 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.37 – 5.29 (**H9, 9', 10'**, m, 3H), 4.99

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(**H10**, d, *J* = 5.5 Hz, 1H), 2.83 (**H3** and **H5**, m, 1H), 2.74 – 2.61 (**H3** and **H5**, **H13**, m, 2H), 2.19 (**H12**, s, 3H), 1.88 – 1.74 (**H2** and **H6**, m, 2H), 1.17 (**H14**, **H14'**, dd, *J* = 14.5, 7.0 Hz, 6H), 1.01 (**H1** and **H7**, t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.75 (C4), 101.85 (C11), 98.10 (C8), 83.10 (C9), 80.96 (C9'), 80.73 (C10'), 79.84 (C10), 36.31 (C3, C5), 30.61 (C13), 22.62 (C14), 22.11 (C14'), 20.70 (C12), 18.59 (C2, C6), 14.39 (C1, C7). (+)ESI-MS (*m*/*z*): ($[M\text{-}Cl]^+$) 677.08.

[Ru_2Cl_2(N^1,N^2-dipentanoylhydrazine)(η^6-*p*-cymene)$_2$] (**4**) – *In situ* formation of ligand. To a solution of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (64 mg, 0.1 mmol) in methanol (8 ml) at room temperature, a solution of pentanoic acid hydrazide (24.6 mg, 0.2 mmol) in methanol (2 ml) was added dropwise. Reaction mixture was stirred for 2.5 h and then left to stand in the fridge for 7 days. The resulting product was filtered off, washed with cold MeOH and dried in air. Yield: 39 mg (53%). Anal. calcd for $C_{30}H_{46}Cl_2N_2O_2Ru_2$: C, 48.71; H, 6.27; N, 3.79. Found: C, 46.65; H, 6.11; N, 3.17. IR (ATR): 3053 (s), 3032 (s), 2961 (s), 2924 (s), 2869 (s), 1536 (s), 1496 (m), 1468 (s), 1389 (s), 1056 (m), 1034 (m), 878 (m). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H 5.32 (**H11, 11', 12'**, m, 3H), 4.98 (**H12**, d, *J* = 5.8 Hz, 1H), 2.87 (**H15,** m, 1H), 2.66 (**H4** and **H6**, m, 2H), 2.18 (**H14**, s, 3H), 1.77 (**H3** and **H7**, m, 2H), 1.43 (**H2** and **H8**, m, 2H), 1.17 (**H16**, **H16'**, t, *J* = 6.6 Hz, 6H), 0.97 (**H1** and **H9**, t, *J* = 8.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ_C 173.88 (C5), 101.83 (C13), 98.11 (C10), 83.03 (C11), 81.27 (C11'), 80.50 (C12), 79.81 (C12'), 34.06 (C4, C6), 30.59 (C15), 29.65 (C3), 29.29 (C7), 22.93 (C16, C16'), 22.52 (C2), 22.12 (C8), 18.56 (C14), 14.03 (C1, C9). (+)ESI-MS (*m*/*z*): ($[M\text{-}Cl]^+$) 704.13.

X-ray crystallography. X-ray diffraction measurements were performed on a Bruker X8 APEXII CCD and Bruker D8-Venture diffractometers. Single crystals were positioned at 40, 34, 35 and 34 mm from the detector and 1784, 1630, 1832 and 2626 frames were measured, each for 10, 30 and 10 s over 1° scan width for **1**, **2**·2EtOH, **3·0.5[RuCl$_2$(η^6-*p*-cymene)]$_2$**, and **4** respectively. The data were processed using SAINT software.[27] Crystal data, data collection parameters, and structure refinement details are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in calculated positions and refined with a riding model. The following computer programs and hardware were used: structure solution, *SHELXS-2013* and refinement, *SHELXL-2013*;[28] molecular diagrams, ORTEP;[29] computer, Intel CoreDuo. Disorder observed for *p*-cymene and alkyl chain of **L^1** in **1** was resolved by applying

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SADI and EADP restraints and DFIX constraints implemented in SHELXL. Crystallographic data for these complexes have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-1492601, -1492600, -1492602 and -1492599. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

Table 1. Crystal Data and Details of Data Collection for **1**, **2**·2EtOH, **3·0.5[RuCl$_2$(η^6-*p*-cymene)]$_2$** and **4**

compound	**1**	**2**·2EtOH	**3·0.5[RuCl$_2$(η^6-*p*-cymene)]$_2$**	**4**
empirical formula	$C_{13}H_{22}Cl_2N_2ORu$	$C_{30}H_{50}Cl_2N_2O_4Ru_2$	$C_{38}H_{56}Cl_4N_2O_2Ru_3$	$C_{30}H_{50}Cl_2N_2O_4Ru_2$
fw	394.30	775.76	1017.86	775.76
space group	$P2_1/c$	P-1	P-1	P-1
a, Å	13.8233(6)	9.0536(4)	9.916(1)	9.6072(5)
b, Å	20.4127(9)	9.0906(4)	12.3781(5)	9.7722(5)
c, Å	12.0459(5)	9.9218(4)	16.9971(7)	17.7727(8)
α, °	103.277(2)	88.9010(11)	76.132(2)	95.264(2)
β, °		88.7726(11)	78.331(2)	90.765(2)
γ, °		85.6563(11)	88.314(2)	93.160(2)
V [Å^3]	3308.2(2)	813.93(6)	1983.2(2)	1658.71(14)
Z	8	1	2	2
λ [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.583	1.583	1.705	1.553
crystal size, mm	0.30 × 0.19 × 0.08	0.25 × 0.21 × 0.11	0.19 × 0.13 × 0.05	0.16 × 0.16 × 0.07
T [K]	100(2)	100(2)	100(2)	100(2)
μ, mm^{-1}	1.265	1.128	1.433	1.107
R_1[a]	0.0315	0.0148	0.0224	0.0335
wR_2[b]	0.0843	0.0386	0.0551	0.0822
GOF[c]	1.044	1.048	1.032	1.058

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Computational Details. The quantum chemical calculations were performed using Gaussian 09 program package.[30] The optimal geometries of the studied molecules were calculated in the gas-phase by DFT method with B3LYP (Becke's three parameter Lee–Yang–Parr) functional[31,32] without any constraints (energy cut-off of 10^{-5} kJ mol^{-1}, final RMS energy gradient under 0.01 kJ mol^{-1} A^{-1}). For all calculations, the SVP/FitSVP basis set was employed.[33,34] The optimised structures were confirmed to be real minima by frequency analysis (no imaginary frequencies). The

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enthalpies and Gibbs free energies were evaluated 298.15 K. Visualisation of the obtained theoretical results was done by Molekel program package.[35]

Conclusion

The formation of *N,N'*diacylhydrazines from hydrazides in the presence of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$, isolated as dinuclear ruthenium(II) complexes was confirmed by spectroscopic and X-ray diffraction methods. A tentative mechanism of these reactions is proposed. The carbon atom of carbonyl group of butyric- or pentanoic acid hydrazide undergoes nucleophilic attack by NH_2 group of another substituted hydrazine, followed by a loss of hydrazine and formation of *N,N'* diacylhydrazine capable to link two ruthenium ions. X-ray crystallography of dinuclear complexes confirmed their pseudo-tetrahedral geometry which is characteristic for all η^6-arene ruthenium complexes. The preparation of these dinuclear ruthenium complexes emphasize the usefulness of *in situ* formation of ligands in preparation of new compounds. The further effort will be directed towards synthesis of higher nuclearity discrete metalla-assemblies.

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Formation of new tetradentate bridging ligands was triggered by the presence of starting diruthenium complexe resulting in the formation of new diruthenium assemblies.