

## **Redox Non-Innocence and Isomer-Specific Oxidative** Functionalization of Ruthenium-Coordinated β-Ketoiminate

Sudip Kumar Bera, Sanjib Panda, Sourajit Dey Baksi, and Goutam Kumar Lahiri<sup>\*[a]</sup>

Abstract: This article deals with isomeric ruthenium complexes [Ru<sup>III</sup>( $L^{R}$ )<sub>2</sub>(acac)] (S = 1/2) involving unsymmetric  $\beta$ -ketoiminates (AcNac) ( $L^{R} = R$ -AcNac, R = H (1), Cl (2), OMe (3); acac = acetylacetonate) [R = para-substituents (H, Cl, OMe) of N-bearing aryl group]. The isomeric identities of the complexes, cct (cis-cis-trans, blue, a), ctc (cis-trans-cis, green, b) and ccc (cis-cis-cis\_ pink, c) with respect to oxygen (acac), oxygen (L) and nitrogen (L) donors, respectively, were authenticated by their single-crystal X-ray structures and spectroscopic/electrochemical features. One-electron reversible oxidation and reduction processes of 1-3 led to the elec-

## Introduction

 $\beta$ -diketiminate<sup>[1]</sup> (NacNac) ligand system has gained profound recent interest from the broader perspectives of coordination/ organometallic chemistry by virtue of its tunable electronic and steric features.<sup>[2–4]</sup> The central  $\beta$ -carbon of metal coordinated NacNac (a vinylogous amidine) is known to be reactive towards electrophiles, which includes cycloaddition with dienophiles to form bicyclic structures, activation of small diatomic molecules (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>) by interacting with their LUMOs, methyl cation migration etc.<sup>[5]</sup> On the contrary, reactivity of metal complexes of analogous heteroditopic  $\beta$ -ketoiminate (AcNac = L) has not been well explored.<sup>[6]</sup> The present article is therefore originated to probe electronic and reactivity aspects of ruthenium coordinated AcNac ligand.

The present report describes synthesis, structural and spectroscopic aspects of isomeric  $[Ru^{III}(L^R)_2(acac)]$  (**a**-**c**) [R = parasubstituents (H, Cl, OMe) of N-bearing aryl group] in 1-3 (Scheme 1). Further, it addresses (i) electronic structural aspects of the complexes in accessible reversible redox states in  $1^n - 3^n$ (n = +, 0, -1), (ii) isomer specific oxidative functionalization of AcNac in 2 b/3 b to yield corresponding 4/4' and (iii) theoretical insights relating to the oxygentaion of  $C_{\beta}$  (diastereotopic face) of AcNac in 2b including the formation of selective diastereomer.

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Green-ctc (b) Pink-ccc(c) Blue-cct (a) 02 <u>R</u> н 1a, 1c : [Ru(acac)(AcNac)2] СІ : 2a, 2b, 2c Redox non-innocence OMe: 3b, 3c Aerobic oxygenation Transition state calculatior <u>R</u> CI : 4 OMe: 4 4/4

tronic formulations of [Ru<sup>III</sup>(L)(L<sup>-</sup>)(acac)]<sup>+</sup> and [Ru<sup>II</sup>(L)<sub>2</sub>(acac)]<sup>-</sup>

for  $1^+-3^+$  (S=1) and  $1^--3^-$  (S=0), respectively. The triplet

state of 1<sup>+</sup>-3<sup>+</sup> was corroborated by its forbidden weak half-

field signal near  $g \approx 4.0$  at 4 K, revealing the non-innocent

feature of L. Interestingly, among the three isomeric forms

(a-c in 1-3), the ctc (b in 2b or 3b) isomer selectively under-

went oxidative functionalization at the central  $\beta$ -carbon (C-

 $H \rightarrow C=O$ ) of one of the L ligands in air, leading to the forma-

tion of diamagnetic  $[Ru^{II}(L)(L')(acac)]$  (L' = diketoimine) in 4/

4'. Mechanistic aspects of the oxygenation process of AcNac

in 2b were also explored via kinetic and theoretical studies.

Scheme 1. Representation of complexes under study.

## **Results and Discussion**

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#### Synthesis, general characterization and structure

Substituted  $\beta$ -ketoimines (R-AcNacH = LH, R = H, Cl, OMe) were prepared from acetylacetone and corresponding para-substituted aniline in refluxing ethanol and in presence of catalytic amount of trifluoroacetic acid.<sup>[7]</sup> Though three tautomeric forms of LH (ketamine, ketimine and enimine) are feasible, the observed sharp and D<sub>2</sub>O exchangeable broad <sup>1</sup>H NMR peaks at  $\delta_{i}$  5.2 ppm and 12 ppm corresponding to methine ( $\beta$ -CH) and hydrogen bonded NH protons, respectively, suggested its ketamine form (Scheme 2).



Scheme 2. Tautomeric equilibria of LH.

Isomeric complexes of [Ru<sup>III</sup>(L)<sub>2</sub>(acac)] (a-c in 1-3, Scheme 1) were prepared by reacting one-equivalent of the metal precursor [Ru<sup>II</sup>(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] with three equivalent of respective R-AcNacH (LH) in presence of excess sodium acetate base under dinitrogen atmosphere followed by their separation on a neutral alumina column. We however failed to observe any trace of the tris-complex ([Ru(L)<sub>3</sub>]) as confirmed by mass spectrometry. This might be due to more steric involvement in the tris-situation as well as relatively less leaving aptitude of the acetylacetonate ligand. The isomeric forms of cct(a), ctc(b) and ccc(c) with respect to oxygen (acac), oxygen (L) and nitrogen (L) donors, respectively, in 1-3 (Scheme 1) were authenticated by their single crystal X-ray structures. All the three isomeric forms  $(cct(\mathbf{a}), ctc(\mathbf{b}), ccc(\mathbf{c}))$  could be isolated for R-AcNac with R=CI (2), while only two isomers cct(a), ccc(c) and ctc(b), ccc(c) were achievable for 1 (R = H) and 3 (R = OMe), respectively (Scheme 1). The presence of three anionic ligands (two AcNac and one acac) possibly facilitated the oxidation of Ru<sup>II</sup> to Ru<sup>III</sup> in 1-3 during the purification process under aerobic condition. Further, methine proton of one of the coordinated L in ctc isomeric **2b** or **3b** selectively oxygenated  $(C-H(L)\rightarrow C=O(L')$  via the activation of aerial oxygen with the concomitant change in metal redox (Ru<sup>III</sup> in **2b** or **3b** versus Ru<sup>II</sup> in **4** or **4**', Scheme 1) due to the stronger  $\pi$ -acceptor feature of L' in **4** or **4**'. Though we failed to obtain suitable single crystals of 4 or 4' to ascertain its molecular structure, their identities were established by other analytical techniques (see later).

The electrically non-conducting **1–4** exhibited satisfactory microanalytical (Experimental Section) and mass spectrometry (Figure S1) data. Isomeric forms of **1–3** were authenticated by single crystal X-ray structures of representative complexes (Figure 1, Table 1 and Figures S2–S3, Tables S1–S3, Supporting Information).

Table 1. Selected bond distances (Å).						
Bond	1a	1c	2a	2 b	3 b	3c
Ru1-N1	2.050(3)	2.038(2)	2.060(2)	2.016(5)	2.0176(17)	2.032(2)
Ru1-N2	2.056(3)	2.012(2)	2.072(2)	2.015(5)		2.039(2)
Ru1-O1	1.992(2)	1.9859(18)	1.9926(19)	2.006(5)	2.0087(14)	2.0229(17)
Ru1-O2	1.993(2)	2.0220(18)	1.9956(18)	2.013(4)	2.0571(15)	1.9994(17)
Ru1-O3	2.031(2)	2.0343(18)	2.0297(18)	2.060(4)		2.0374(17)
Ru1-04	2.033(2)	2.0644(18)	2.0272(18)	2.049(4)		2.0528(17)
C2-N1	1.310(4)	1.318(3)	1.312(4)	1.340(8)	1.333(3)	1.331(3)
C9-N2	1.319(4)	1.323(4)	1.311(4)	1.345(8)		1.325(3)
C4-01	1.297(4)	1.289(3)	1.291(3)	1.289(8)	1.287(3)	1.286(3)
C7-02	1.299(4)	1.280(4)	1.306(3)	1.296(7)		1.298(3)
C2-C3	1.413(5)	1.410(4)	1.422(4)	1.414(9)	1.413(3)	1.408(4)
C3-C4	1.372(5)	1.376(4)	1.381(4)	1.377(10)	1.378(3)	1.385(4)
C7-C8	1.373(5)	1.381(4)	1.364(4)	1.394(9)		1.378(4)
C8-C9	1.415(5)	1.404(4)	1.436(4)	1.410(9)		1.417(4)

The N,O donors of monoanionic AcNac (L) ligand formed a six-membered chelate with the average bite angle of  $\approx 92^{\circ}$ . The average C2–N1, C2–C3, C3–C4, C4–O1 and C9–N2, C9–C8, C8–C7, C7–O2 bond lengths in **1–3** suggested the delocalization of negative charge over the AcNac backbone as in the case of acac. The shorter Ru-N(L) distance *trans* to Ru-O(acac) bond in *ctc* or *ccc* isomer as compared to that *cis* to Ru-O(acac) in *cct* isomer could be attributed to the impact of



Figure 1. ORTEP diagrams with ellipsoids at 50% probability level. H-atoms are omitted for clarity.

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trans effect exerted by the  $\sigma$ -donating acac ligand. The isomeric identity (**a**–**c**, Scheme 1) of the complexes was reflected in *cis* and *trans* N1-Ru1-N2 or N1-Ru1-N1' angles involving two AcNac in *ctc/ccc* and *cct* forms, respectively, due to the difference in connectivity of the donor atoms as well as spatial orientation of the pendant phenyl rings.

Ruthenium(III) ( $t_{2g}^{5}$ , S = 1/2) derived isomeric **1–3** displayed broad and ill-defined proton resonances<sup>[8,9]</sup> (Experimental Section) corresponding to the full molecule over a wide chemical shift region in CDCl<sub>3</sub> owing to paramagnetic contact shift effect,<sup>[10]</sup> which indeed had restricted to assign the individual proton signals. Interestingly, an appreciable downfield shifting of the proton resonances appeared on moving from *ctc*(**b**) to *cct*(**a**) to *ccc*(**c**) isomeric form due to the varying orientation of the pendant phenyl rings. In agreement with the Ru<sup>III</sup> center, isomeric forms **a–c** (**1–3** in Scheme 1) displayed metal based anisotropic EPR (Figure 2, Table 2 and Figure S4, Supporting Information).



Figure 2. X-band (9 GHz) EPR spectra in  $CH_2Cl_2/toluene$  (1:5) for 2a, 2b, 2c and in  $CH_3CN$  for  $2a^+$ ,  $2b^+$ ,  $2c^+$  at 4 K.

Table 2. EPR data at 4 K.						
Complex	<i>g</i> <sub>1/2</sub>	<b>g</b> 1	<b>g</b> <sub>2</sub>	<b>g</b> 3	$<\!g\!>^{\scriptscriptstyle{[a]}}$	$\Delta g^{\mathrm{[b]}}$
2 a+[c]	4.40	2.25	2.11	1.87	2.08	0.38
2 a <sup>[d]</sup>		2.25	2.18	1.80	2.08	0.45
2 b <sup>+[c]</sup>	4.33	2.24	2.11	1.88	2.08	0.36
2 b <sup>[d]</sup>		2.32	2.06	1.79	2.06	0.53
2c <sup>+[c]</sup>	Not resolved	2.23	2.18	1.85	2.09	0.38
2 c <sup>[d]</sup>		2.29	2.13	1.85	2.07	0.44
[a] < g > = 1 CH <sub>2</sub> Cl <sub>2</sub> -tolue	$\{(1/3)  (g_1^2 + g_2^2 + g_2^2) = (1:5).$	$(g_3^2)$ } <sup>1/2</sup> .	$[b] \Delta g = g$	g <sub>1</sub> —g <sub>3</sub> . [a	:] In CH₃CN.	[d] In

#### Electrochemistry and electronic structure

Isomeric **a-c** in **1–3** displayed well defined quasi-reversible one oxidative (O1) and one reductive (R1) couples in the potential ranges of 0.74 to 0.84 V and -0.81 to -0.86 V versus SCE, respectively (Figure 3, Table 3). The minor cathodic wave associ-

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Figure 3. Cyclic (black) and differential pulse (green) voltammograms in  $CH_3CN$ .

Table 3. Electrochemical data. <sup>[a]</sup>				
Complex	<i>E</i> ⁰[V] (Δ <i>E</i> <sub>p</sub> [mV]) <sup> </sup> Ο1	ы R1	<i>K</i> <sub>c</sub> <sup>[c]</sup>	
1a	0.70(70)	-0.92(90)	2.8×10 <sup>27</sup>	
1c	0.63(140)	-0.97(160)	1.3×10 <sup>27</sup>	
2a	0.83(130)	-0.81(160)	6.2×10 <sup>27</sup>	
2b	0.84(140)	-0.80(170)	6.2×10 <sup>27</sup>	
2c	0.74(200)	-0.86(220)	1.3×10 <sup>27</sup>	
3b	0.72(70)	-0.88(80)	1.3×10 <sup>27</sup>	
3c	0.55(90)	-0.98(100)	8.5×10 <sup>25</sup>	
[a] From cyclic voltammetry in CH <sub>3</sub> CN/0.1 M Et <sub>4</sub> NClO <sub>4</sub> at 100 mV s <sup>-1</sup> . [b] Potential in V versus SCE; peak potential differences $\Delta E_p$ [mV] (in parentheses). [c] Comproportionation constant from <i>RT</i> In $K_c = nF(\Delta E)$ , <sup>[11]</sup> $K_c$ between O1 and R1.				

ated with the oxidation process (O1) at around -0.2 V for **1a** or **2a** was originated due to its slight irreversible feature, which was therefore absent in the separately scanned reduction process (Figure S5, Supporting Information).

One-electron nature of the couple was confirmed by constant potential coulometry. Oxidation (O1) or reduction (R1) potential of the complexes varied systematically based on the electron withdrawing and donating properties of R associated with the AcNac(L) moiety and it followed the order of CI > H > OMe. Though isomeric forms cct(**a**) and ctc(**b**) exhibited close by redox potentials, slight negative shift of redox potential was apparent for the ccc(**c**) isomer (Table 3). The significantly large  $K_c$  value of  $\approx 10^{27}$  for the intermediate state corroborated the fact of the stable form of the isolated **1–3** (Scheme 1).





Figure 4. Spin density representation (Isosurface value 0.003).

The pertinent question of involvement of metal or ligand or mixed metal/ligand based frontier orbitals in the redox processes of the isomeric forms  $\mathbf{a}-\mathbf{c}$  in  $\mathbf{1}^n-\mathbf{3}^n$  (n=+1, 0, -1) was ascertained via the collective consideration of MO compositions (Tables S4-S28, Supporting Information) and EPR (Figure 2, Table 2 and Figure S4, Table S29, Supporting Information)/Mulliken spin distribution (Figure 4, Table 4 and Figure S6,

Table 4. DFT ca ties.	alculated (UB3LYP/LanL2	DZ/6-31G*)Mulliken	spin densi-
Complex	Ru	AcNac	acac
2a <sup>+</sup> (S=1)	1.167	0.678	0.153
<b>2</b> a (S = 1/2)	0.801	0.174	0.025
2 b <sup>+</sup> (S = 1)	1.127	0.711	0.162
<b>2 b</b> (S = 1/2)	0.778	0.203	0.019
2c <sup>+</sup> (S=1)	1.233	0.526	0.241
<b>2</b> c (S=1/2)	0.764	0.221	0.015

Table S30, Supporting Information) at the paramagnetic states. This suggested selective one-electron oxidation of one of the AcNac (L) ligands leading to the electronic structural form of  $[Ru^{III}(L)(L^{\bullet})(acac)]^+$  for  $1^+-3^+$  (S = 1) instead of alternate feasible formulation of [Ru<sup>IV</sup>(L)<sub>2</sub>(acac)]<sup>+</sup>. Interestingly, spin density distribution for the oxidized form of the isomers (a-c) in  $1^+-3^+$ also revealed that the unpaired spin on AcNac was evenly distributed among both the AcNac moieties due to spin-hopping factor.<sup>[12]</sup> The electronic formulation of electrogenerated oxidized state of  $[Ru^{III}(L)(L^{*})(acac)]^{+}$  (S = 1, 1<sup>+</sup>-3<sup>+</sup>) was also corroborated by its EPR feature at 4 K which displayed forbidden weak half-field signal near  $g \approx 4.0$  corresponding to its triplet (S=1) state<sup>[13]</sup> in addition to metal based anisotropic  $q \approx 2.0$ signal.<sup>[14]</sup> The increase in ligand contribution in the singly occupied molecular orbitals (SOMOs) on moving from 1-3 (S = 1/2) to  $1^+-3^+$  (S = 1) was also reflected in the decreasing g anisotropy ( $\Delta g$  in Table 2 and Table S29, Supporting Information).<sup>[15]</sup> The MO compositions however attributed to the metal based reduction leading to the electronic structural form of  $[Ru^{II}(L)_{2}(acac)]^{-}$  for  $1^{-}-3^{-}$  (S = 0). This indeed reemphasized the redox non-innocent potential of AcNac particularly with respect to the electron removal process as was also demonstrated recently for the symmetric NacNac under analogous coordination situation.  $^{\rm [5b,\,16]}$ 

Electronic spectral data of 1-3 are set in Table 5. The change in spectral profile on oxidation as well as reduction for each of the isomeric species (**a**–**c**) (Figure 5 and Figure S7, Supporting Information) was analyzed by TD-DFT calculations (Table S31, Supporting Information).

Table 5. Electronic spectral data in CH <sub>3</sub> CN.			
Complex	$\lambda$ [nm] [ $\epsilon/M^{-1}$ cm <sup>-1</sup> ]		
1a 1c 2a 2b 2c 3b 3c	303(20 000), 340(15 200), 585(1800) 300(13 800), 365(8000), 573(1800) 300(35 400), 343(23 400), 594(3200) 267(31 400), 296(30 200), 362(14 200), 658(3400) 265(11 400), 300(10 800), 365(6000), 569(1800) 267(11 800), 293(10 800), 364(5200), 648(1200) 266(10 600), 298(9800), 367(5800), 572(1600)		

In general, isomeric complexes (a-c in 1-3) exhibited similar spectral profile in CH<sub>3</sub>CN with one moderately intense visible band and multiple intense transitions in the higher energy UV region, where band position and intensity varied reasonably as a function of their isomeric identities. Similarly, slight variation of band position and intensity occurred on moving from 1 to 3. TD-DFT calculations for the ruthenium(III) derived 1-3 suggested that the visible and UV-region transitions corresponded to the mixed ligand/metal to metal/ligand and intra/interligand charge transfer transitions, respectively. The lowest energy visible transition underwent appreciable red shifting on moving from 1-3 to  $1^+-3^+$ , which could be assigned to ligand to metal/ligand based charge transfer transition. On the other hand, slight blue shifting of the visible band had taken place for the one-electron reduced ruthenium(II) derived  $1^--3^-$ , which was assigned to be L targeted metal-to-ligand charge transfer transition.

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**Figure 5.** Experimental (CH<sub>3</sub>CN) and TD-DFT ((U)B3LYP/CPCM/CH<sub>3</sub>CN) calculated electronic spectra of  $2^n$  (n = 0, +1, -1). Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of 2000 cm<sup>-1</sup>.

#### **Oxidative functionalization**

*cct*(**a**) and *ccc*(**c**) isomeric forms of **1–3** (Scheme 1) were found to be perfectly stable in air. However, *ctc*(**b**) analogue in **2b** or **3b** (Scheme 1) selectively underwent oxidative functionalization at the central β-carbon (C–H→C=O) of one of the L ligands on prolonged exposure to air with the concomitant reduction in metal oxidation state from ruthenium(III) to ruthenium(II) in diamagnetic [Ru<sup>II</sup>(L)(L')(acac)] (L' = diketoimine) (**4** or **4**'). This might be due to the increase in nucleophilicity of the reactive C<sub>β</sub> center of AcNac originated through electron pushing from the σ-donating acac *trans*- to AcNac nitrogens.

Though both **2b** and **3b** could be transformed to the corresponding **4** (Scheme 3), the detailed characterization was performed for the chloro derivative. Interestingly, free AcNac remained unaltered under the similar reaction condition, implying the effective role of metal coordination towards its functionalization process.

The electrically neutral and Ru<sup>II</sup> derived diamagnetic **4** gave satisfactory microanalytical (Experimental Section) and mass spectrometric (Figure 6 and Figure S1, Supporting Information) data and displayed well defined proton resonances within the standard chemical shift region of  $\delta$ , 0–10 ppm (Figure S8, Supporting Information). The transformation of C–H  $\rightarrow$  C=O of one of the L ligands on moving from **2b** to **4** was also evident in



Scheme 3. Selective oxygenation of ctc isomer.



Figure 6. Experimental and simulated ESI(+) mass spectra of  $\{4\}^+$  in  $CH_3CN$ .

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Figure 7. Overlapping IR spectra of 2b (in black) and 4 (in red) as KBr disc.



Figure 8. Electronic spectra of 2 b and 4 in acetonitrile.

the appearance of a new  $\nu$ (C=O) vibration at 1640 cm<sup>-1</sup> (Figure 7) and their distinct electronic spectral features (Figure 8) with respect to the parent **2b**. The visible and UV-region bands were assigned based on the TD-DFT calculations (Table S31, Supporting Information) as L/L' targeted mixed metal/ligand to ligand based and intra/inter ligand charge transfer transitions, respectively.



Figure 9. Cyclic (black) and differential pulse (green) voltammograms of 4 in  $CH_3CN$ .

Ruthenium(II) derived **4** showed reversible one-electron oxidation(O1) and reduction(R1) (Figure 9) primarily corresponding to Ru<sup>II</sup> $\rightarrow$ Ru<sup>III</sup> (**4**<sup>+</sup>) and L' $\rightarrow$ L'<sup>-</sup> (**4**<sup>-</sup>), respectively, as supported by MO compositions (Table S4, Supporting Information) and spin density plots (Figure 10). The metal and ligand (L') dominated spins in **4**<sup>+</sup> and **4**<sup>-</sup> were corroborated by their characteristic anisotropic ( $g_1$ : 2.44,  $g_2$ : 2.13,  $g_3$ : 1.73,  $\Delta g$ : 0.71, <g>:



Ru: 0.676, L': 0.263

Ru: 0.05, L': 0.933

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**Figure 10.** Spin density representation of  $\mathbf{4}^n$  (n = +1, -1; S = 1/2) (isosurface = 0.003).



Figure 11. X-band (9 GHz) EPR spectrum of 4<sup>-</sup> in CH<sub>3</sub>CN at 100 K.



**Figure 12.** Change in spectral profile of  $2b \rightarrow 4$  conversion in CH<sub>3</sub>CN at 333 K. Rate is calculated based on the growing feature at 540 nm (Inset).

2.12) and isotropic EPR (*g*: 2.003) spectral features,<sup>[14]</sup> respectively (Figure 11 and Figure S9, Supporting Information).

Spectrophotometric monitoring of the oxygenation of **2b** to **4** (Figure 12 and Figure S10, Supporting Information) at 333 K suggested a pseudo 1<sup>st</sup> order rate process with the rate constant (*k*) value of  $6.3 \pm 0.1 \times 10^{-6} \text{ s}^{-1}$ . First order and zero<sup>th</sup> order rates with respect to substrate and molecular oxygen, respectively, suggested reorganization of the Ru-complex via the interaction with O<sub>2</sub> at the rate determining step. Slower rate of conversion of **2b**  $\rightarrow$  **4** even at 333 K ( $\approx$ 3 days) indeed restricted us to follow it at variable temperature to understand the reaction kinetics by UV-vis spectroscopy. This however could be illustrated by transition state calculations (Scheme 4, Figures 13–14).

Initial approach of triplet oxygen  $({}^{3}\Sigma_{g}^{-})$  to the methine position of one of the AcNac moieties in **2b** (*S*=1/2) generates transient superoxide intermediate (*S*=1/2), which undergoes faster H-shuttling followed by homolytic cleavage of the O–O

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Scheme 4. Formation of diastereomeric intermediates.

bond to yield **4** and hydroxyl radical byproduct.<sup>[5b]</sup> Hydroxyl radical which has generated in the reaction medium rapidly quenched to some other stable forms. Moreover, unsymmetrical feature of AcNac backbone facilitates to form a diastereotopic face at the reactive  $C_{\beta}$ -center. Thus, the approach of oxygen molecule from the upward (*Si*) and downward (*Re*) directions leads to diastereomeric intermediates with 'S' (I) and 'R' (II) configurations, respectively, at the chiral  $C_{\beta}$  center (Scheme 4). However, *Re* face interaction is calculated to be kinetically preferred due to lower activation barrier ( $\Delta G_1^{\neq}/\Delta G_2^{\neq}$  for *Re* and *Si*: 39.2/13.6 and 41.8/14.7 kcal mol<sup>-1</sup>, respectively, at 298 K, where  $\Delta G_1^{\neq}$  and  $\Delta G_2^{\neq}$  correspond to respective activation barriers for **2 b** $\rightarrow$ I1 and I1 $\rightarrow$ **4** conversions, Figure 13). That indeed results in thermodynamically stable product that



**Figure 13.** Gibbs free energy ( $\Delta G$  at 298 K) profile for the oxygenation of Ru-coordinated AcNac using UB3LYP/LANL2DZ/6-31G\* level of theory. Associated  $\Delta G/\Delta H$  are shown in each state.  $\Delta G$  of starting substrates is taken as zero. Subscript *Re/Si* suggests the different approach of  ${}^{3}O_{2}$  at the diastereotopic face (C<sub>β</sub>).

is, diketoimine (L') in **4** ( $\Delta G_{Product}$  for *Re* and *Si*: -3.1 and -1.1 kcal mol<sup>-1</sup>, respectively, Figure 13). This can be considered as the consequence of steric factor exerted by the adjacent phenyl ring of another AcNac for the *Si* face. This in turn disfavors the approach of O<sub>2</sub> at the *Si* face as has also been supported by bond length variation in TS1 (C<sub>β</sub>-O: 1.953 (*Si*) and 1.775 (*Re*), Figure S11, Supporting Information). Further, different spin orientation on O<sub>2</sub> attack results in greater peroxide character in the superoxide radical (I1) for the *Si* face as is reflected in higher spin accumulation on the oxygen unit (*Re/Si*: 0.919/0.816) as well as in bond length variation (Figure 14). Highly endergonic ( $\Delta G^{\neq}_{298K} \sim 40$  kcal mol<sup>-1</sup>) process of **2**b $\rightarrow$  [TS]<sup> $\neq$ </sup> $\rightarrow$ I1 makes it the rate determining step (Figure 13) which may be the consequence of decrease in entropy ( $\Delta S^{\neq} \sim -36$  cal mol<sup>-1</sup> K<sup>-1</sup>) as well as endothermic nature of the reac-



Figure 14. Selected bond parameters, frontier molecular orbital (isosurface = 0.06) and spin density (SD) (isosurface = 0.003) plots, calculated at UB3LYP level. Hydrogen and chlorine atoms are removed for clarity.

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tion  $(\Delta H^{\neq} \sim 30 \text{ kcal mol}^{-1})$  due to the O=O bond weakening during the adduct formation. However, the overall transformation,  $2\mathbf{b} \rightarrow \mathbf{4}$  is exergonic in nature due to the incorporation of stable C=O into the AcNac backbone. The higher kinetic barrier is supportive of the experimentally observed slower conversion rate. The use of M06L functional (Figures S12–S13 and Table S32, Supporting Information) extends similar trend in energy for the conversion sequence with lower activation barrier  $(\Delta G_1^{\neq} / \Delta G_2^{\neq} \text{ for } Re: 33.1/11.2 \text{ kcal mol}^{-1}$ , in acetonitrile at 333 K, i.e., under the experimental condition). The failure of complex  $\mathbf{4}$  (S=0) in participating further oxygenation process involving its other AcNac moiety can be attributed to higher kinetic barrier  $(\Delta G^{\neq} = 46.2 \text{ kcal mol}^{-1} \text{ at UB3LYP level}, Fig$ ure S14, Supporting Information) for its interaction with the $singlet oxygen <math>({}^{1}\Delta_{0})$ .

The selective interaction of  $\pi_{1g}^*$ -HOMOs of triplet dioxygen with the  $C_\beta$  center of AcNac in **2b** can be rationalized by the fact of AcNac dominated  $\alpha$ -SOMO (Figure 14). The alternate intermediate involving peroxo bridging (Ru-O-O- $C_\beta$ )<sup>[18]</sup> is however failed to converge possibly due to the formation of unfavorable seven coordinated Ru.

## Conclusions

The present article highlighted structural, spectroelectrochemical, electronic structural and reactivity aspects of isomeric (*cct*, *ctc*, *ccc*) paramagnetic complexes [Ru<sup>III</sup>(AcNac)<sub>2</sub>(acac)] (**a**–**c** in **1–3**, Scheme 1). The collective consideration of experimental and theoretical events revealed selective involvement of AcNac-based orbitals in the oxidation process ( $1-3 \rightarrow 1^+-3^+$ ), attributing its redox non-innocence. In conjunction, selective participation of *ctc*-isomeric **2b** or **3b** in the aerobic oxidation process (central  $\beta$ -carbon of L, C–H→C=O) revealed the unexplored oxygenation profile of AcNac. Further, the mechanistic pathway for the oxygenation process in **2b** including selective formation of one diastereomer has been attributed with the help of transition state theory.

## **Experimental Section**

#### Materials

The precursor complex *cis*-[Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>[19]</sup> and  $\beta$ -ketoamines (R-AcNacH=LH, R=H, Cl, OMe) were prepared according to the literature procedures.<sup>[7]</sup> Other reagents and chemicals were obtained from Aldrich and used as received. HPLC grade solvents were employed for spectroscopic and other electrochemical studies.

#### **Physical measurements**

FT-IR spectra were recorded on a Nicolet spectrophotometer with samples prepared as KBr pellets. Cyclic voltammetry measurements of the complexes ( $\approx 10^{-3}$  M) were performed using a PAR model 273A electrochemistry system. Glassy carbon working electrode, platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used as a standard three-electrode configuration cell. Constant potential coulometry experiment was performed by using a platinum wire-gauze working electrode. Et<sub>4</sub>NClO<sub>4</sub> was used as the supporting electrolyte. All electrochemi-

cal experiments were carried out under a dinitrogen atmosphere. Half-wave potential  $E^0 = 0.5(E_{pa} + E_{pc})$ , where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic cyclic voltammetry peak potentials, respectively. UV-vis spectroelectrochemical studies were performed on a BAS SEC2000 spectrometer system. UV-vis spectral studies were performed on a PerkinElmer Lambda 950 spectrophotometer. The elemental analyses were carried out on a Thermoquest (EA 1112) microanalyzer. Electrospray mass spectrometry (ESI-MS) was carried out on a Bruker's Maxis Impact (282001.00081) spectrometer. <sup>1</sup>H NMR were recorded using Bruker Avance III 400 MHz spectrometer. The EPR measurements of coulometrically generated species (substrate concentration 0.1 m) were made with a Bruker system ESP300 spectrometer or JEOL model FA200 spectrometer.

#### **Kinetic studies**

Kinetic experiments were carried out under  $O_2$  atmosphere (excess) by dissolving **2b** (5×10<sup>-5</sup> M) in CH<sub>3</sub>CN. The change in absorbance at 540 nm for **2b**  $\rightarrow$ **4** was monitored for the rate calculation. The pseudo-first order (due to excess oxygen) rate constant (*k*) for **2b**  $\rightarrow$ **4** conversion was calculated based on non-linear exponential fit in Origin Pro8 software by following the equation:  $y=y_0+A_1 \times$ exp( $-x/t_1$ ), where *y*,  $y_0$  and *x* corresponded to absorbance at 540 nm at time *t*, *t*=0 and time period (t in min) over which the absorption change took place, respectively. A<sub>1</sub> represented pseudo-first order coefficient and the value of pseudo-first order rate constant (*k* in s<sup>-1</sup>) was [1/( $t_1 \times 60$ )].

#### Crystallography

Single crystals of 1a, 1c, 2a, 2b and 3b, 3c were grown by slow evaporation of their 2:1 dichloromethane-n-hexane and 2:1 dichloromethane-methanol solutions, respectively. X-ray crystal data were collected on a Rigaku Saturn-724 + CCD single crystal diffractometer using Mo-K $_{\alpha}$  radiation. The data collection were carried out by standard  $\omega\mbox{-scan}$  technique and were evaluated and reduced by using CrystalClear-SM Expert software. Absorption correction (numerical) was applied to the collected reflections. The structures were solved by direct method using SHELXS-97 and refined by full matrix least-squares with SHELXL-2014/7, refining on F<sup>2.[20]</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. Hydrogen atoms were included in the refinement process as per the riding model. CCDC 1908644 (1a), 1908645 (1c), 1908646 (2a), 1908647 (2b), 1908648 (3b), and 1908649 (3c) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

#### **Computational details**

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Full geometry optimizations were carried out by using density functional theory method at the (R)B3LYP (for 1<sup>*n*</sup> (*n*=-1), 2<sup>*n*</sup> (*n*=-1), 3<sup>*n*</sup> (*n*=-1), and 4<sup>*n*</sup> (*n*=0)) or (U)B3LYP (for 1<sup>*n*</sup> (*n*=0, +1), 2<sup>*n*</sup> (*n*=0, +1), 3<sup>*n*</sup> (*n*=0, +1)) and 4<sup>*n*</sup> (*n*=+1,-1)), level with Gaussia an 09 program package.<sup>[21]</sup> Except ruthenium all other elements were assigned the 6-31G\* basis set. The LANL2DZ basis set with effective core potential was employed for the ruthenium atom in all cases. Vertical electronic excitations based on optimized geometries were computed using the time-dependent density functional theory<sup>[22]</sup> (TD-DFT) formalism in acetonitrile using the conductor-like polarizable continuum model (CPCM). Electronic spectra were calculated using the SWizard program.<sup>[23,24]</sup> Chemissian<sup>[25]</sup> 1.7 was

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used to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures were visualized with ChemCraft.<sup>[26]</sup>

Transition state calculations were performed at B3LYP/(U)B3LYP level of theory starting from infinitely separated substrates. Single imaginary frequency for the transition states (TSs) and real frequencies for local minima were obtained. The connectivity of each TS was validated through a relaxed potential energy surface scan for the corresponding reaction coordinate, and was found to be the highest-energy point that connected the relevant reactant and product. The zero-point vibrational energies, thermal corrections were obtained from the harmonic frequency calculations at the B3LYP/(U)B3LYP level of theory. Results obtained from (U)B3LYP functional were also tested with M06L density functional.

#### **Preparation of complexes**

#### Synthesis of [Ru(acac)(AcNac)<sub>2</sub>] (1-3)

Isomeric complexes  $\mathbf{a}-\mathbf{c}$  in  $\mathbf{1}-\mathbf{3}$  (Scheme 1) were prepared by reacting three-equivalent of respective R-AcNacH (R=H (1), Cl (2), OMe (3)) with one-equivalent of Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> and three-equivalent of sodium acetate base in refluxing ethanol under dinitrogen atmosphere for 8 h. Solvent of the reaction mixture was evaporated to dryness under reduced pressure. The separation of isomers in each case (1–3, Scheme 1): **a** (blue), **b** (green), **c** (pink), was performed on a neutral alumina column by using 2:1, 3:1, 4:1 dichloromethane-petroleum ether mixtures, respectively. Evaporation of solvent under reduced pressure gave pure complexes.

**1a:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.26 mmol), H-AcNacH (136 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 36 mg (25%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**1a**}<sup>+</sup> calcd: 549.13; found: 549.14; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =20.82, 6.28, 5.15, 3.96, 2.50, 2.37, 2.16, 1.22, -1.06, -7.71 ppm; IR (KBr pellet):  $\tilde{\nu}$ =1575 cm<sup>-1</sup>( $\nu$ (C= O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$ =4 Ω<sup>-1</sup> cm<sup>2</sup> м<sup>-1</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>Ru: C 59.11, H 5.70, N 5.10; found: C 59.32, H 5.87, N 5.38.

**1 c:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.26 mmol), H-AcNacH (136 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 22 mg (15%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**1 c**}<sup>+</sup> calcd: 549.13; found: 549.12. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.40, 16.37, 14.42, 13.71, 9.70, 7.44, 5.78, 2.54, 2.38, 2.19, 2.01, -17.36, -19.19, -23.88 ppm; IR (KBr pellet):  $\tilde{\nu}$  = 1570 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$ = 3 Ω<sup>-1</sup> cm<sup>2</sup> m<sup>-1</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>31</sub>N<sub>2</sub>O<sub>4</sub>Ru: C 59.11, H 5.70, N 5.10; found: C 59.23, H 5.71, N 5.34.

**2a:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.26 mmol), Cl-AcNacH (165 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 49 mg (30%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**2a**}<sup>+</sup> calcd: 617.04; found: 617.06. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 12.60$ , 8.59, 5.55, 5.31, 2.09, 1.25, 0.91, -2.76, -24.23, -26.98; IR (KBr pellet):  $\tilde{\nu} = 1570 \text{ cm}^{-1}(\nu(\text{C=O}))$ ; molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\text{M}} = 4 \ \Omega^{-1} \text{cm}^{2} \text{M}^{-1}$ ; elemental analysis calcd (%) for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>Ru: C 52.51, H 4.73, N 4.53; found: C 52.65, H 5.12, N 4.90.

**2 b:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.26 mmol), Cl-AcNacH (165 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 24 mg (15%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**2 b**+Na}<sup>+</sup> calcd: 640.04; found: 640.08. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.04, 8.80, 5.10, 1.27, 0.91, -5.56, -6.18, -13.73 ppm; IR (KBr pellet):  $\tilde{\nu}$  = 1578 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$  = 6  $\Omega^{-1}$  cm<sup>2</sup>  $M^{-1}$ ; elemental analysis calcd (%) for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>Ru: C 52.51, H 4.73, N 4.53; found: C 52.79, H 5.09, N 4.31.

**2 c:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.78 mmol), Cl-AcNacH (165 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 41 mg

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(25%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**2 c**+Na}<sup>+</sup> calcd: 640.04; found: 640.04. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =17.71, 16.85, 14.46, 13.45, 10.12, 9.51, 2.59, 2.38, 2.22, 1.28, 0.93, -17.86, -21.27, -24.78, -31.36 ppm; IR (KBr pellet):  $\tilde{\nu}$ =1572 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$ =4  $\Omega^{-1}$  cm<sup>2</sup> м<sup>-1</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>Ru: C 52.51, H 4.73, N 4.53; found: C 52.85, H 4.82, N 4.68.

**3 b:** Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.78 mmol), OMe-AcNacH (160 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 32 mg (20%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**3 b**+Na}<sup>+</sup> calcd: 632.05; found: 632.14. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.13, 10.13, 7.40, 6.86, 3.68, 2.52, 1.49, 1.28, 0.89, -4.34, -5.19, -5.53 ppm; IR (KBr pellet):  $\tilde{\nu}$  = 1575 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$  = 4 Ω<sup>-1</sup> cm<sup>2</sup> m<sup>-1</sup>; elemental analysis calcd (%) for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O<sub>6</sub>Ru: C 57.23, H 5.80, N 4.60; found: C 57.59, H 5.94, N 4.43.

**3 c**: Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (100 mg, 0.26 mmol), OMe-AcNacH (160 mg, 0.78 mmol), NaOAc (64 mg, 0.78 mmol), EtOH (40 mL). Yield: 30 mg (18%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {**3 c**}<sup>+</sup> calcd: 609.06; found: 609.14. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.04, 8.82, 5.12, 1.38, 0.90, -0.5.57, -6.20, -13.77 ppm; IR (KBr pellet):  $\tilde{\nu}$  = 1570 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$ =3  $\Omega^{-1}$  cm<sup>2</sup> м<sup>-1</sup>; elemental analysis calcd (%) for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O<sub>6</sub>Ru: C 57.23, H 5.80, N 4.60; found: C 57.45, H 5.63, N 4.51.

#### Synthesis of $[Ru^{II}(L)(L')(acac)]$ (L' = diketoimine) (4)

Complex **2b** was sensitive to air and irreversively transformed to the corresponding **4**. Complex **4** was therefore achieved by vigorous purging of oxygen for about 24 h in ethanolic solution (15 mL) of **2b** at 70° C, which was then purified on a neutral alumina column using  $CH_2CI_2$  as eluent.

**4: 2b** (50 mg, 0.08 mmol), EtOH (10 mL). Yield: 28 mg (55%). MS (ESI+, CH<sub>3</sub>CN): *m/z* {[**4**]}<sup>+</sup> calcd: 632.12; found: 632.13; <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 7.37 (4H, aromatic), 7.18 (2H, aromatic), 6.95 (1H, aromatic), 6.58 (1H, aromatic), 5.24 (1H, C<sub>β</sub>-H of acac), 5.16 (1H, C<sub>β</sub>-H of L), 2.92 (6H, 2CH<sub>3</sub>), 2.16 (3H, CH<sub>3</sub>), 1.85 (6H, 2CH<sub>3</sub>), 1.64 ppm (3H, CH<sub>3</sub>); IR (KBr pellet):  $\tilde{\nu}$  = 1640 cm<sup>-1</sup>( $\nu$ (C=O)); molar conductivity (CH<sub>3</sub>CN):  $\Lambda_{\rm M}$  = 3  $\Omega^{-1}$  cm<sup>2</sup> M<sup>-1</sup>; elemental analysis calcd (%) for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>Cl<sub>2</sub>Ru: C 51.25, H 4.46, N 4.43; found: C 51.55, H 4.57, N 4.31.

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** oxidative functionalization  $\cdot$  redox non-innocence  $\cdot$  ruthenium  $\cdot$  spectroelectrochemistry  $\cdot \beta$ -ketoiminate

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# **FULL PAPER**



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Redox Non-Innocence and Isomer-Specific Oxidative Functionalization of Ruthenium-Coordinated β-Ketoiminate

Proven guilty: The redox non-innocence and selective oxygenation profile of  $\beta$ -ketoiminate (AcNac) in an isomeric (*ctc/cct/ccc*) ruthenium platform have been attributed.