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Reactions of ketones with coordinated nitriles on β-diketonato ruthenium complexes leading to formation of compounds with new carbon–carbon bonds

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Abstract

The reactions of $[Ru(acac)_2(CH_3CN)_2]$ with four ketones (acetone, ethyl methyl ketone, acetylacetone and monochloroacetone), and the reactions of $[Ru(acac)_2(C_6H_5CN)_2]$ with two ketones (acetone and ethyl methyl ketone) yielded six novel compounds of β-ketiminato ruthenium complexes: $[Ru(acac)_2(mhmk)]$, $[Ru(acac)_2(ehmk)]$, $[Ru(acac)_2(mAmk)]$, $[Ru(acac)_2(mClmk)]$, $Ru(acac)_2(mhbk)]$, and $[Ru(acac)_2(ehbk)]$ (mhmk = 4-iminopentane-2-one mono anion, ehmk = 5-iminohexane-3-one mono anion, mAmk = 3-(1-iminoethyl)-2,4-pentanedione mono anion, mClmk = 3-chloro-4-imino-pentane-2-one mono anion, mhbk = 1-phenyl-1-iminobutane-3-one mono anion, ehbk = 1-phenyl-1-iminopentane-3-one mono anion). All the new complexes have been characterized by elemental analyses, ^1H NMR, MS and electronic spectral data. Crystal and molecular structures for the six β-ketimine complexes have been solved by single crystal X-ray diffraction studies. A mechanism involving the attack of ketones on the coordinated nitrile has been proposed. The electrochemical redox behavior of the β-ketimine complexes has been elucidated.

Keywords: Bis(acetylacetonato)bis(acetonitrile)ruthenium complex; β-Ketimine; Reaction of ligated nitrile; Ketone; Cyclic voltammetry

1. Introduction

Nitriles are isoelectronic with N_2, CO, isocyanide and alkynes and they have been known to form transition metal complexes. Owing to their weak σ and π-acceptor ability, these samples can be easily substituted to give a variety of coordination and organometallic compounds. Among the reactions, those on coordinated nitriles leading to the formation of other organic compounds have attracted the attention of chemists for quite some time due to the occurrence of insertion and coupling reactions and nucleophilic and electrophilic attacks [1]. Recently, the reactions of H_2O and CH_3OH on coordinated nitrile in a nitrosyl ruthenium complex have been reported to give imido-type complexes [2]. Moreover, hydrolysis of nitriles to amide has been shown to be enhanced by the coordination of nitriles to various metal centers [3]. The formation of β-diketimine chelate has been reported by prior insertion of nitrile into a M–C bond before the attack of nucleophilic methylene at the electrophilic carbon of the other coordinated nitrile on scandium [4]. Chromium alkyls react with an excess of nitrile to form mononuclear β-diketiminato complexes by a similar

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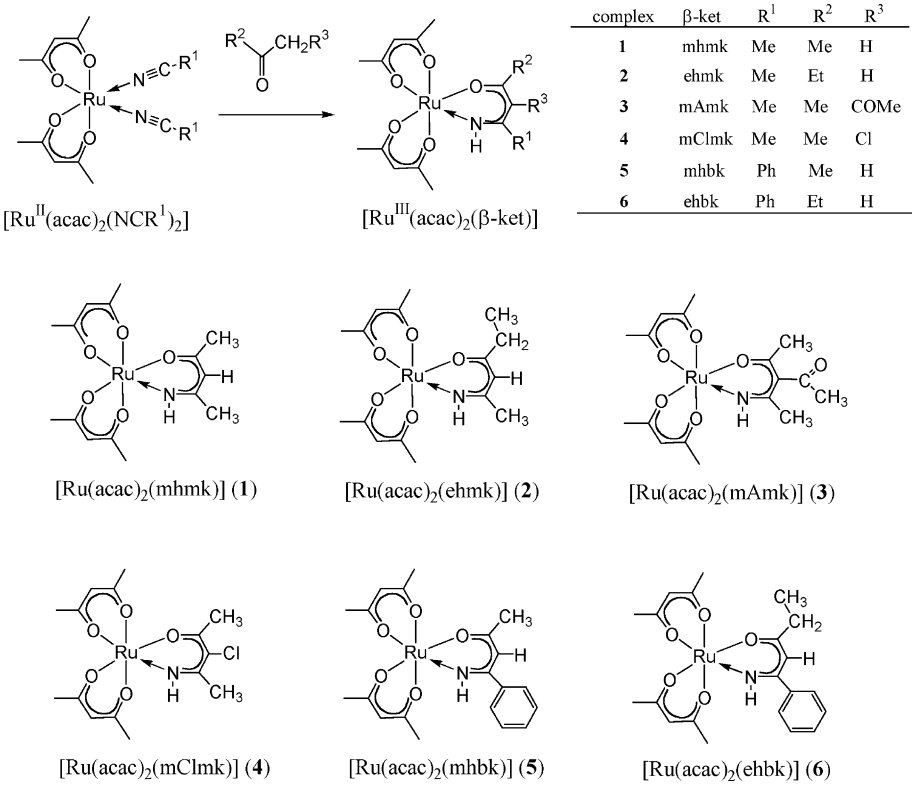
insertion of nitrile into the Cr–C bond [5]. Very reactive methylidenetitanocene reacts with nitrile to yield β-diketiminato complex [6]. Oxo- and sulfidozirconocene intermediates, [Cp*ZrX] (X = O, S), cycloadd nitriles to form six-membered metallocycles via initial formation of aza-oxo-metallacycle, followed by subsequent insertion of a second nitrile into the Zr–N bond [7]. Nakamura and co-workers [8] have reported the formation of β-ketimine chelates by the reaction of *cis*- and *trans*-[$PtCl_2(NCPh)_2$] with thallium acetylacetonate complex by a mechanism involving the nucleophilic attack of the β-diketonate carbanion on the coordinated nitrile carbon atom. This is probably the first known direct attack of the coordinated nitrile leading to the formation of β-ketimine chelate as all other reactions involve nitrile insertion into M–C bond prior to the attack on coordinated nitrile. Only one β-ketimine chelate formation has been reported on rhenium by the attack of 2-oxoalkyl group on coordinated nitrile [9]. Though vinylimido complexes react with unsaturated organic species allowing cross coupling of nitriles with ketones to afford new carbon–carbon bonded compounds, no such reaction of acetone on coordinated nitrile ligand has been shown to give such compounds [6,10]. Moreover, to our knowledge there is no report of a reaction of ketone on coordinated nitrile ligand leading to β-ketimine with new C–C bond formation. Hence, we report in this paper the reactions of various ketones on the coordinated nitrile in a β-diketonato ruthenium complex with the formation of β-ketiminate. We have reported a short communication about the reaction of acetone on coordinated acetonitrile in β-diketonato ruthenium complex ([$Ru(acac)_2(CH_3CN)_2$]) with the formation of β-ketiminato complex [11]. These reactions, besides being novel, are not only the first report of the reaction of a ketone on the coordinated nitrile ligand but also are a new and simple method for the formation of β-ketimine on ruthenium ion.

2. Results and discussion

2.1. Reactions of coordinated nitrile with ketone

The reactions of ketones (acetone, methylethyl ketone, monochloroacetone, and acetylacetone) with the ruthenium precursors, [$Ru(acac)_2(AN)_2$] or [$Ru(acac)_2(BN)_2$] (AN, acetonitrile; BN, benzonitrile) yielded the six novel compounds (**1**–**6**) with new carbon–carbon bonds (Fig. 1). The reaction of diethyl ketone with [$Ru(acac)_2(AN)_2$] or [$Ru(acac)_2(BN)_2$] did not produce any β-ketiminato complex. Furthermore, the methylene group, except in the methyl group adjacent to carbonyl in methyl ethyl ketone, monochloroacetone, and acetylacetone group, did not react with carbon in nitrile. These results suggested that only the methyl carbon adjacent to carbonyl in ketone can make the C–C bond



complex	β-ket	R^1	R^2	R^3
1	mhmk	Me	Me	H
2	ehmk	Me	Et	H
3	mAmk	Me	Me	COMe
4	mClmk	Me	Me	Cl
5	mhbk	Ph	Me	H
6	ehbk	Ph	Et	H

Fig. 1. The formation reactions of the β-ketiminato ruthenium(III) complexes and their structural formulas.

with the carbon in nitrile. These reactions are quite novel as these can be best described as reactions between a coordinated ketone and a coordinated nitrile on a complex. This is probably the first report on the reactions of ketone on coordinated nitrile with the formation of β-ketiminato chelate though such a chelate was obtained elsewhere [4] by prior insertion of nitrile into M–C bond before the attack on coordinated nitrile. However, a rhenium enolate complex, $[(CO)_4(PPh_3)Re(H_2CCOOC_2H_5)]$, on reaction with PPh_3 in the presence of trimethylamine oxide and acetonitrile yielded a β-ketiminato complex [9]. The mechanism proposed for this formation involves a rearrangement of enolate from carbon bonding to one with oxygen bonding prior to the formation of β-ketiminate.

On careful examination of all the reactions of various ketones with $[Ru(acac)_2(AN)_2]$ or $[Ru(acac)_2(BN)_2]$, it appears that the presence of an electron withdrawing group on the carbon atom of the ketone which attacks the coordinated nitrile is necessary for the formation of β-ketiminate. This has been further confirmed by the fact that diethyl ketone, which contains an electron-donating methyl group, does not react with $[Ru(acac)_2(AN)_2]$. Moreover, deprotonation of coordinated ketone and oxidation of ruthenium are necessary steps for the formation of a nucleophile, and the reaction is facilitated by an electron-withdrawing group on the carbon atom. Based on the above observations and on the structures of the complexes formed, the mechanism shown in Fig. 2 has been suggested. The first step is the coordination of ketone by the replacement of one of the coordinated nitriles (step 1). A nucleophilic center could be generated by the deprotonation of an alkyl group (step 2). The process is facilitated by the presence of electron withdrawing group on it and by the tautomerism of coordinated ketone. The coordinated ketones react with the coordinated nitrile on the ruthenium complex, leading to the formation of β-ketiminato chelates with new carbon–carbon bond (step 3). Then, the migration of H^+ from the carbon to nitrogen and the oxidation of ruthenium(II) to (III) may take place (step 4). A similar mechanism has been proposed for the diketiminate formation on scandium [4]. However, it is to be pointed out that a direct reaction takes place between water and the coordinated nitrile on ruthenium nitrosyl complex with the formation of methylcarboxyimidato complex [2], where water attacks the electophilic nitrile carbon.

2.2. Structures of β-ketiminato complexes

The crystal and molecular structures of all new complexes except $[Ru(acac)_2(mhmk)]$ (**1**), which has been reported [11], have been determined by single crystal X-ray diffraction studies. Three selected ORTEP plots are given in Figs. 3–5. All the crystal structure data

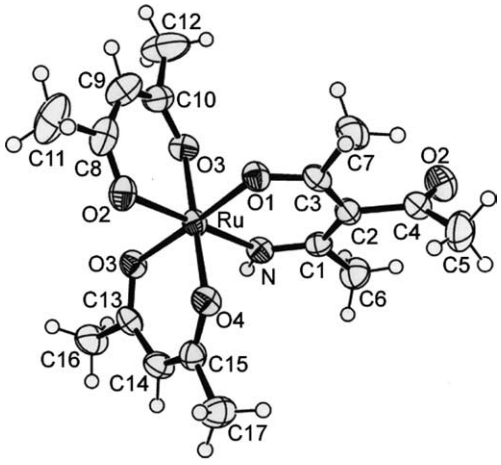


Fig. 3. Molecular structure of $[Ru(acac)_2(mAmk)]$ (**3**).

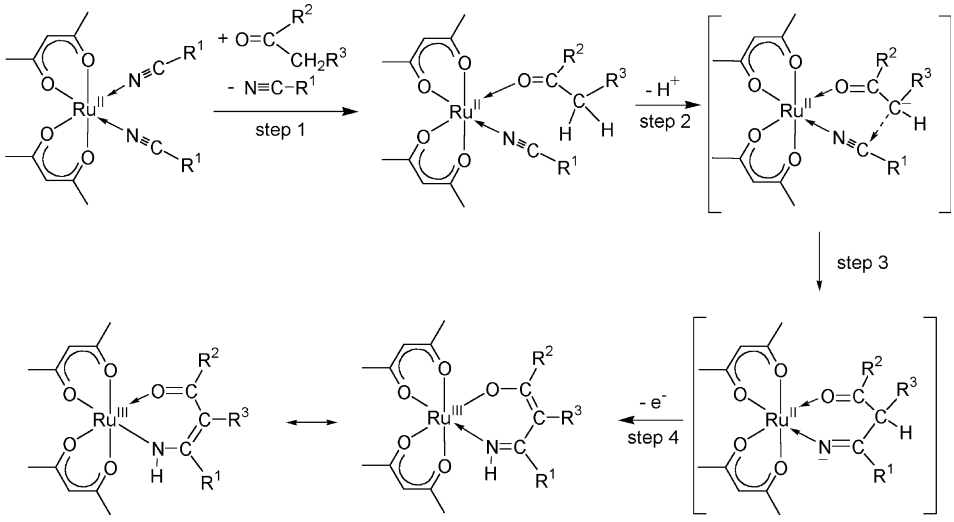


Fig. 2. A presumed formation scheme of β-ketiminato ruthenium(III) complexes with the reaction between $[Ru(acac)_2(RCN)_2]$ (R = CH_3 or C_6H_5) and ketones.

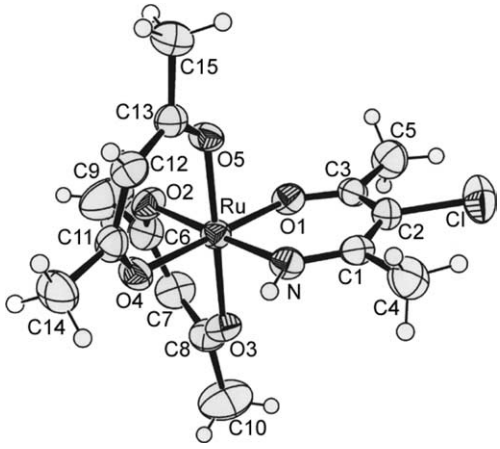


Fig. 4. Molecular structure of [Ru(acac)$_2$(mClmk)] (**4**).

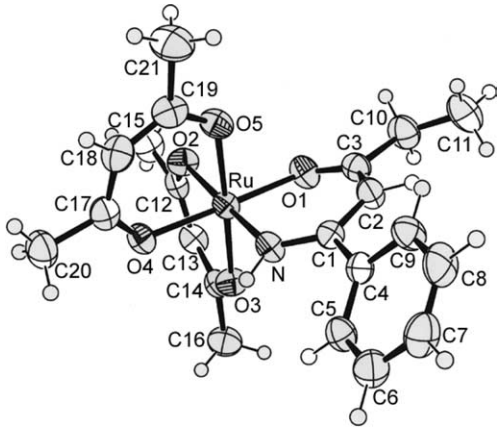


Fig. 5. Molecular structure of [Ru(acac)$_2$(ehbk)] (**6**).

are given in Table 1 and the important bond lengths and bond angles are given in Tables 2–6. The structures of all the complexes can be described as distorted octahedrons with β-ketiminate ligand and ruthenium atom in almost one plane. The general structural features are very similar to that of [Ru(acac)$_3$] [12] and there seems to be no difference in structures irrespective of different substituents on the β-ketiminate chelate rings. The Ru–O lengths observed for acac and that of β-ketiminate are almost the same in all the complexes. However, the Ru–N distance is slightly shorter and is similar to the distance found in salen complexes [10]. The C–O bond lengths of β-ketiminate ligand are slightly longer than the C–O lengths seen in acetylacetonate. The C–N bond length in β-ketiminate is exactly the same as that of C–O (1.29 Å). However, a C–N distance of 1.303 Å has been

Table 2
Selected bond lengths (Å) and angles (°) of [Ru(acac)$_2$(ehmk)] (**2**)

Bond length (Å)		Bond angle (°)	
Ru–N	1.983(3)	O2–Ru–N	178.6(1)
Ru–O1	1.999(2)	O1–Ru–O4	177.52(9)
Ru–O2	2.078(3)	O3–Ru–O5	178.82(7)
Ru–O3	2.034(3)	O2–Ru–O3	91.32(9)
Ru–O4	2.023(3)	O4–Ru–O5	91.97(8)
Ru–O5	2.003(3)	O1–Ru–N	92.1(1)
N–C1	1.302(5)	Ru–N–C1	125.9(3)
C1–C2	1.416(6)	N–C1–C2	122.4(4)
C2–C3	1.365(6)	C1–C2–C3	127.4(4)
O1–C3	1.291(5)	C2–C3–O1	126.3(4)
C1–C4	1.513(6)	C3–O1–Ru	122.6(2)
C3–C5	1.518(7)		

Table 1
Crystallographic data for β-ketiminato complexes

Complexes	[Ru(acac)$_2$(ehmk)] (**2**)	[Ru(acac)$_2$(mAmk)] (**3**)	[Ru(acac)$_2$(mClmk)] (**4**)	[Ru(acac)$_2$(mhbk)] (**5**)	[Ru(acac)$_2$(ehbk)] (**6**)
Formula	$C_{16}H_{24}NO_5Ru$	$C_{17}H_{24}NO_6$ Ru	$C_{15}H_{21}NO_5ClRu$	$C_{20}H_{24}NO_5Ru$	$C_{42}H_{52}N_2O_{10}Ru_2$
Formula weight	411.44	439.45	431.86	459.48	947.02
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Color of crystal	red	red	brown	red	red
Unit cell dimensions					
a (Å)	8.648(6)	9.778(1)	9.113(2)	9.7438(2)	10.142(3)
b (Å)	11.115(8)	10.309(1)	10.234(2)	10.0464(4)	11.931(4)
c (Å)	11.906(9)	11.189(2)	11.387(3)	11.6869(1)	18.418(6)
α (°)	104.849(5)	109.771(3)	113.094(5)	80.957(13)	98.863(4)
β (°)	108.781(5)	110.217(4)	108.080(5)	66.709(9)	98.435(4)
γ (°)	108.676(5)	96.712(2)	93.554(4)	81.81(1)	98.699(4)
Z	2	2	2	2	2
V (Å^3)	940.5(12)	960.5(2)	907.9(3)	1033.66(5)	2143.3(13)
D_{calc} (g cm^{-3})	1.453	1.519	1.580	1.476	1.467
F_{000}	422.00	450.00	438.00	470.00	972.00
μ(Mo Kα) (cm^{-1})	8.55	8.47	10.32	7.87	7.62
T (°C)	25	25	25	25	25
R_1 (>2.00)	0.040	0.039	0.061	0.044	0.049
R (all data)	0.044	0.042	0.072	0.052	0.062
R_w (all data)	0.097	0.096	0.121	0.100	0.102
GOF	0.985	1.035	0.943	0.918	0.856

Table 3
Selected bond lengths (Å) and angles (°) of [Ru(acac)$_2$(mAmk)] (**3**)

Bond length (Å)		Bond angle (°)	
Ru–N	1.971(3)	O3–Ru–N	178.40(8)
Ru–O1	1.988(2)	O1–Ru–O5	177.6(1)
Ru–O3	2.072(3)	O4–Ru–O6	179.91(9)
Ru–O4	2.025(2)	O3–Ru–O4	90.62(9)
Ru–O5	2.019(2)	O5–Ru–O6	91.40(8)
Ru–O6	2.004(2)	O1–Ru–N	91.28(9)
N–C1	1.308(4)	Ru–N–C1	128.0(2)
C1–C2	1.431(3)	N–C1–C2	122.8(3)
C2–C3	1.393(5)	C1–C2–C3	125.3(3)
O1–C3	1.291(4)	C2–C3–O1	126.1(2)
C1–C6	1.512(5)	C3–O1–Ru	126.0(2)
C2–C4	1.510(5)		
C4–O2	1.220(5)		
C4–C5	1.485(4)		
C3–C7	1.513(4)		

Table 4
Selected bond lengths (Å) and angles (°) of [Ru(acac)$_2$(mClmk)] (**4**)

Bond length (Å)		Bond angle (°)	
Ru–N	1.970(3)	O2–Ru–N	178.3(1)
Ru–O1	1.983(3)	O1–Ru–O4	178.9(1)
Ru–O2	2.060(4)	O3–Ru–O5	178.4(1)
Ru–O3	2.020(3)	O2–Ru–O3	90.7(1)
Ru–O4	2.017(3)	O4–Ru–O5	91.5(1)
Ru–O5	1.997(3)	O1–Ru–N	91.7(1)
N–C1	1.312(7)	Ru–N–C1	127.5(3)
C1–C2	1.418(6)	N–C1–C2	121.6(5)
C2–C3	1.389(7)	C1–C2–C3	128.3(5)
O1–C3	1.288(5)	C2–C3–O1	123.8(4)
C1–C4	1.513(8)	C3–O1–Ru	126.5(3)
C3–C5	1.507(6)		
C2–Cl	1.760(6)		

Table 5
Selected bond lengths (Å) and angles (°) of [Ru(acac)$_2$(mhbk)] (**5**)

Bond length (Å)		Bond angle (°)	
Ru–N	1.983(3)	O2–Ru–N	176.21(9)
Ru–O1	1.997(2)	O1–Ru–O4	177.70(9)
Ru–O2	2.073(3)	O3–Ru–O5	179.7(1)
Ru–O3	2.032(2)	O2–Ru–O3	90.68(9)
Ru–O4	2.014(2)	O4–Ru–O5	92.67(9)
Ru–O5	2.000(2)	O1–Ru–N	92.6(1)
N–C1	1.314(4)	Ru–N–C1	124.5(2)
C1–C2	1.413(4)	N–C1–C2	122.7(3)
C2–C3	1.384(5)	C1–C2–C3	127.6(3)
O1–C3	1.277(4)	C2–C3–O1	125.9(3)
C1–C4	1.488(5)	C3–O1–Ru	123.6(2)
C3–C10	1.518(5)		

observed in rhodium ketiminate complex [13], which contains a phenyl group on the nitrogen atom. The Ru–O length *trans* to Ru–N is slightly longer than other Ru–O lengths in all the complexes. This may be due to the fact that there is less back bonding into O than into N, which are *trans* to each other. The bond lengths of O1–C3 and N–C1 in all the complexes are in between those for single and for double bonds, indicating the presence of alternative single and double bonds in the β-ketiminato ring. The C1–C2 bond lengths are longer than that of C2–C3, corresponding to single and double bonds, respectively. All the above observations confirm that there is delocalization of electrons in the β-ketiminato ring.

2.3. ^1H NMR spectra of β-ketiminato complexes

The ^{1}H NMR spectral data and the assignments are given in the experimental section. The chemical shifts for all the complexes have been observed over a wide range up to −34.60 ppm. This is characteristic of paramagnetic shifts due to the presence of Ru^{III}, which is a d^5 system with one unpaired electron. There are many factors apart from electron density that affect the chemical shifts of these systems. Especially in the case of mixed ligand complexes, both metal–ligand interactions and ligand–ligand interactions have to be considered. The paramagnetic shifts in all the ruthenium(III) complexes can arise from both the contact interaction and the pseudo-contact interaction [14]. All the methyne proton signals have been shifted to upper field from the corresponding signals of the diamagnetic ruthenium(II) complexes [15–17]. The methyl protons of the acac showed singlets in the range from 5.70 to −6.31 ppm and those of the β-ketiminate showed singlets around −12.58 to −22.4 ppm. The methyne protons of acac showed two types of singlets in the range from 0.26 to −15.2 ppm and from −16.35 to −29.7 ppm for the presence of two types of acac in the complexes. The methyl protons of β-ketiminate showed singlets in the range from −28.2 to −34.6 ppm. In the case of the ethyl group in the β-ketiminate, the signal due to the terminal methyl protons has been shifted to lower field (4.63–8.15 ppm) due to the effect of the ring current. The signal due to the presence of phenyl group has also been shifted to lower field (5.58–10.32 ppm). The methyl protons of the γ-acetyl group showed a singlet at 12.5 ppm. No signal could be observed either for the proton on the nitrogen atom or the methyne proton of the β-ketiminate though the former could be due to the fast exchange of proton with deuterium.

2.4. Electronic spectra of β-ketiminato complexes

The electronic spectra of the complexes have been measured either in acetonitrile or in dichloromethane. The band positions and their molar absorption coefficients are given in Table 7. The general features of the electronic spectra are the same as those of [Ru(acac)$_3$] [18]. Three to four bands have been observed in the range from 573 to 240 nm for the complexes. The bands

Table 6
Selected bond lengths (Å) and angles (°) of [Ru(acac)$_2$ (ehbk)] (**6**)

Bond length (Å)			Bond angle (°)		
Ru–N	1.986(2)	1.976(3)	O2–Ru–N	177.2(1)	177.0(1)
Ru–O1	1.996(2)	1.999(3)	O1–Ru–O4	177.52(7)	176.3(1)
Ru–O2	2.058(2)	2.072(2)	O3–Ru–O5	177.32(8)	178.95(9)
Ru–O3	2.027(2)	2.041(2)	O2–Ru–O3	91.10(8)	90.60(9)
Ru–O4	2.016(2)	2.023(3)	O4–Ru–O5	92.74(9)	92.50(8)
Ru–O5	2.011(2)	1.996(2)	O1–Ru–N	91.65(9)	91.5(1)
N–C1	1.316(3)	1.324(4)	Ru–N–C1	126.1(1)	125.2(2)
C1–C2	1.417(4)	1.410(5)	N–C1–C2	122.2(2)	122.3(3)
C2–C3	1.383(4)	1.383(5)	C1–C2–C3	127.2(3)	126.6(4)
O1–C3	1.287(3)	1.282(5)	C2–C3–O1	125.8(3)	125.7(4)
C1–C4	1.497(4)	1.495(5)	C3–O1–Ru	124.1(2)	122.3(3)
C3–C10	1.528(5)	1.525(8)			
C10–C11	1.503(5)	1.40(1)			

Table 7
Electronic spectral data of β-diketonato- and β-ketiminato complexes in acetonitrle

Complexes	λ_{max} (nm) ($\log_{10}(\epsilon/mol^{-1}\ dm^3\ cm^{-1})$)			
β-Diketonato complexes				
[Ru(acac)$_3$] [19]		271 (4.18)	347 (3.87)	505 (3.16)
[Ru(acac)$_2$(BN)$_2$]	227 (4.49)	270 (4.45)	391 (4.25)	
[Ru(acac)$_2$(bhma)]	248 (sh)	290 (4.27)	353 (sh)	502 (3.22)
β-Ketiminato complexes				
[Ru(acac)$_2$(mhmk)] (**1**) [11]		274 (4.38)	351 (4.13)	559 (3.69)
[Ru(acac)$_2$(ehmk)] (**2**)		272 (4.26)	344 (3.97)	530 (3.65)
[Ru(acac)$_2$(mAmk)] (**3**)		272 (4.21)	350 (3.93)	546 (3.30)
[Ru(acac)$_2$(mClmk)] (**4**)		271 (4.15)	358 (3.92)	591 (3.25)
[Ru(acac)$_2$(mhbk)] (**5**)	240 (4.08)	272 (4.16)	370 (3.86)	570 (2.95)
[Ru(acac)$_2$(ehbk)] (**6**)	242 (4.06)	273 (4.16)	373 (3.86)	571 (3.00)

around 570 and 350 nm have been assigned to MLCT transitions and the bands around 250 nm to LMCT transitions.

2.5. Electrochemistry of β-ketiminato complexes

The cyclic voltammograms of all the β-ketiminato complexes are shown in Fig. 6; these are almost identical in nature except for their redox potentials. Analyses of the cyclic voltammograms showed that both the oxidation and reduction reactions were reversible one-electron transfer processes corresponding to $Ru^{III} \rightarrow Ru^{IV}$ and $Ru^{III} \rightarrow Ru^{II}$, respectively. The reversible half-wave potentials ($E_{1/2}$) of the oxidation and the reduction are given in Table 8. The $E_{1/2}$ of the oxidation process was in the range from 0.36 to 0.44 V and reduction process was in the range from −1.23 to −1.36 V. The $E_{1/2}$ of the β-ketiminato complexes showed significant negative shifts in their reductions as well as their oxidations when compared to those of corresponding β-diketonato complexes. The large negative shifts are attributable to the replacement of O donor atom by NH donor group in β-ketiminate ligand. This may be explained by the difference in electronegativity between N and O atoms. The electronegativity of N atom is less compared to that of O atom; hence, there may be higher electron density on ruthenium containing β-ketiminate ligand compared to the density on acetylacetonate ligand. In other words, the ring consisting of ruthenium and β-ketiminate (O^N) has higher electron density than the ring consisting of ruthenium and acetylacetonate (O^O). Fig. 7 was the substituent effects of the β-ketiminate on $E_{1/2}$ together with that of β-diketonate. Linear relationships were obtained between $E_{1/2}$ value and the sum of Hammett constant ($\sum\sigma_{pmp}$ [19]) of the substituents on the β-diketonate and β-ketiminate in the complexes as well as in the case of β-diketonato complexes. Here, σ_{pmp} represents a combination of the Hammett constants for the *meta* (σ_m) and the *para* position (σ_p) [20]. Furthermore, the slopes of the straight lines for $E_{1/2}$ (ox) and $E_{1/2}$ (red) against $\sum\sigma_{pmp}$ (β-diketonato complex: oxidation = 0.30 V; reduction = 0.16 V, β-ketiminato complexes: oxidation = 0.34 V; reduction = 0.18 V) were nearly the same for β-diketonato and β-ketiminato complexes. Furthermore, the C–C bond lengths of β-ketiminate in the β-diketonato ruthenium(III) complexes were

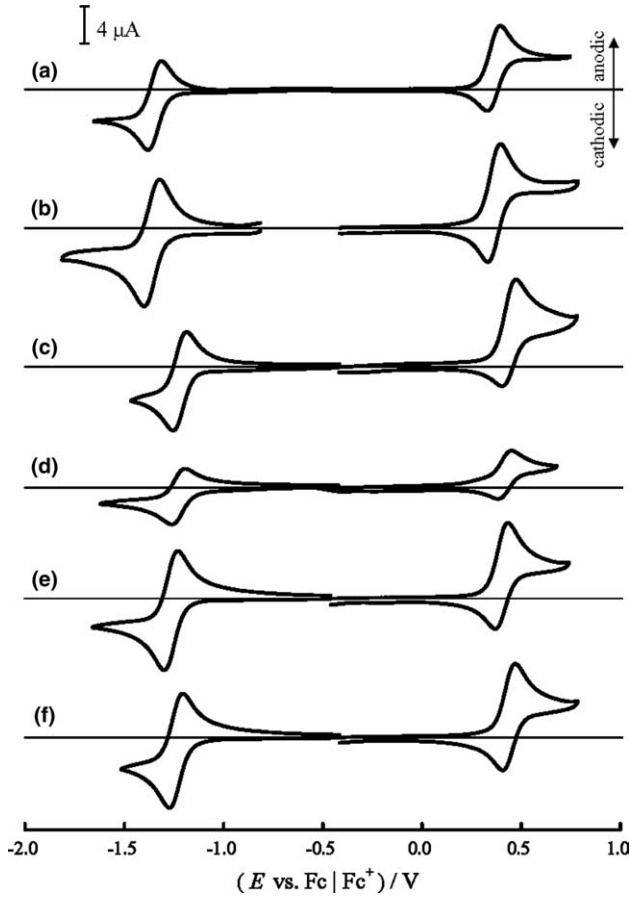


Fig. 6. Cyclic voltammograms of β-ketiminato ruthenium complexes in acetonitrile solution containing 0.1 mol dm^{-3} tetraethylammonium perchlorate. Potential scan rate = 0.1 V s^{-1}. The concentration of complexes except complex **4** is 1 mmol dm^{-3}. The concentration of complex **4** is 0.5 mmol dm^{-3}. (a) $[Ru(acac)_2(ehmk)]$ (**1**); (b) $[Ru(acac)_2(ehmk)]$ (**2**); (c) $[Ru(acac)_2(mAmk)]$ (**3**); (d) $[Ru(acac)_2(mClmk)]$ (**4**); (e) $[Ru(acac)_2(mhbk)]$ (**5**); (f) $[Ru(acac)_2(ehbk)]$ (**6**).

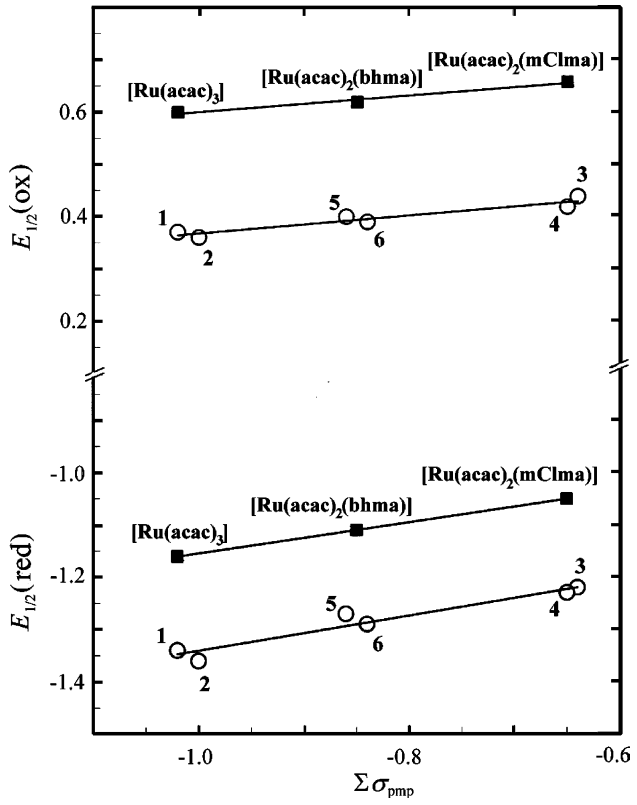


Fig. 7. Dependence of $E_{1/2}$ on $\sum\sigma_{pmp}$. $\sum\sigma_{pmp}$ is the sum of Hammett substituent constants [19,20] on β-ketiminate (○) or β-diketonate (■). Slope (β-ketiminate): oxidation; 0.18 V, reduction 0.34 V. Slope (β-diketonato): oxidation; 0.16 V, reduction; 0.30 V.

Table 8
Reversible half-wave potentials ($E_{1/2}$[a] of the β-diketonato- and β-ketiminato complexes in 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$–CH_3CN at 25 °C and $\sum\sigma_{pmp}$[b][19])

Complexes	$\sum\sigma_{pmp}$	$E_{1/2}$(red) (V)	$E_{1/2}$(ox) (V)
β-Diketonato complexes			
$[Ru(acac)_3]$	−1.02	−1.16	0.60
$[Ru(acac)_2(bhma)]$	−0.85	−1.11	0.62
$[Ru(acac)_2(mClma)]$ [19]	−0.65	−1.11	0.62
β-Ketiminato complexes			
$[Ru(acac)_2(mhmk)]$ (**1**) [11]	−1.02	−1.34	0.37
$[Ru(acac)_2(ehmk)]$ (**2**)	−1.00	−1.36	0.36
$[Ru(acac)_2(mAmk)]$ (**3**)	−0.64	−1.22	0.44
$[Ru(acac)_2(mClmk)]$ (**4**)	−0.65	−1.23	0.42
$[Ru(acac)_2(mhbk)]$ (**5**)	−0.86	−1.27	0.40
$[Ru(acac)_2(ehbk)]$ (**6**)	−0.84	−1.29	0.39

[a] vs. $Fc|Fc^+$.

[b] $\sum\sigma_{pmp} = \sum\sigma_p$ (for β-position substitutes) + $\Sigma\sigma_m$ (for γ-position substitutes) [19].

between single and double bonds. Such results mean that the six member ring consisting of ruthenium(III) and β-ketiminate is conjugated as well as that of ruthenium(III) and β-diketonate.

3. Experimental

3.1. General

For synthetic experiments, commercially available reagent grade solvents and chemicals were used. $[Ru(acac)_2(AN)_2]$ was prepared by the literature methods [21–23] and $[Ru(acac)_2(BN)_2]$ was prepared by a similar method, as described in the syntheses section. Spectroscopic grade acetonitrile from Dojin Chemical Laboratories was used for spectroscopic work. Dehydrated acetonitrile and dichloromethane from Kanto Chemical Co. Inc., were used for voltammetric studies. The supporting electrolyte, tetraethylammonium perchlorate (TEAP) (special polarographic grade), was purchased from Nakarai Chemicals Co. Ltd.

^1H NMR spectra were recorded in $CDCl_3$ with a JEOL Lambda Spectrophotometer ($SiMe_4$ as internal reference). UV–Vis spectra were recorded on a Hitachi

Model U-3210 spectrometer. IR spectra were recorded with a Shimadzu FT-IR-8600PC spectrophotometer and EI- and FAB-MS spectra were measured with a JEOL JMS-SX102A spectrometer.

The voltammograms were measured with BAS100W (BAS Corp.). All the voltammograms were measured in 0.1 mol dm^{-3} TEAP–AN and dichloromethane (DM) solutions and all the potentials were measured against Ag|AgCl (3 mol dm^{-3} aqueous NaCl solution) reference electrode obtained from BAS Corp. The reference electrode was connected to the test solution through 0.1 mol dm^{-3} TEAP–AN or DM solution with a Vycor plug filled with the supporting electrolyte solution. All the electrode potentials were determined against the half-wave potential of the ferrocene/ferricinium$^+$ ($Fc|Fc^+$) couple as an internal standard. The average potential of the reference electrode at 25 °C was −0.47 V in AN and −0.52 V in DM. A platinum disk of diameter 1.6 mm embedded in Teflon from BAS Corp was used as the test electrode. A spiral platinum wire was used as the auxiliary electrode. The reversible half-wave potentials were determined from the mid-point potential of cyclic voltammograms, $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the potentials of the anodic and cathodic peaks, respectively.

3.2. X-ray crystallography

Crystal data and structure determination parameters are given in Table 1. Single crystals of the complexes suitable for diffraction studies were grown by the vapor diffusion of *n*-hexane into a solution of the complex in benzene or dichloromethane. Single crystal data collections were performed at 298 K with a Rigaku AFC8 Mercury-CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.7170 Å) radiation. The data were collected and processed using the CrystalClear software package of Rigaku Corp [24]. The structures were solved by direct methods [25] or Patterson methods [26] and were expanded using Fourier techniques [27]. For all complexes, empirical absorption corrections were applied using Lorentz-polarization and absorption. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStucture crystallographic software packages [28,29].

3.3. Syntheses

3.3.1. Preparation of *[Ru(acac)$_2$(bhma)]*

[Ru(acac)$_2$(bhma)] (Hbhma = 1-phenyl-1,3-butanedione). To a solution of [Ru(acac)$_2$(AN)$_2$] (0.30 g, 0.79 mmol) in ethanol (100 cm^3), 0.38 g (2.36 mmol) of 1-phenyl-1,3-butanedione (Hbhma) was added, then the mixture was heated under reflux for 30 min. After it was cooled to room temperature, an aqueous solution of $KHCO_3$ (1.2 mol dm^{-3}) was added and the mixture was refluxed for 30 min. Then, the solvent was evaporated and the residue was chromatographed on a silica gel column. The red fraction eluted with toluene/2-propanol (4:1 v/v) was collected and chromatographed again. The red fraction obtained by eluting with toluene/2-propanol (29:1 v/v) yielded the red crystals of [Ru(acac)$_2$(bhma)]. Yield: 0.25 g (68% based on Ru). FAB-Mass: m/z^+ = 460 (M^+). *Anal.* Calc. for $C_{20}H_{23}O_6Ru$ (460.46): C, 52.17; H, 5.03. Found: C, 52.97; H, 4.99%.

3.3.2. Preparation of *[Ru(acac)$_2$(C$_6$H$_5$CN)$_2$]*

1.0 g (2.5 mmol) of [Ru(acac)$_3$] was dissolved in a mixture of ethanol–water (14:1 v/v, 150 cm^3) and then 0.52 g (5.0 mmol) of benzonitrile was added to the solution. The solution was refluxed with stirring for 10 min under an argon atmosphere. Zn powder activated with hydrochloric acid was added to the resulting solution. The solution color turned from red to brown. Then, the solution was refluxed for 30 min. The solvent was then evaporated under vacuum and the residue was chromatographed on silica gel column. Brown crystals. Yield: 1.26 g (97% based on Ru). FAB-Mass: m/z^+ = 506 (M^+), 403 ($M–C_6H_5CN$). FT-IR: $\nu(C{\equiv}N)$ = 2197 cm^{-1}. *Anal.* Calc. for $C_{24}H_{24}N_2O_4Ru$ (505.53): C, 57.02; H, 4.79; N, 5.54. Found: C, 57.25; H, 4.63; N, 5.36%. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.82, 1.88 (each s, 3H, acac's β-CH_3), 4.64 (s, 2H, acac's γ-H), 7.35, 7.41, 7.62 (10H, phenyl–H of BN).

3.3.3. Preparation of *[Ru(acac)$_2$(β-ket)]*

Six novel compounds of β-ketimine complexes, [Ru(acac)$_2$(β-ket)] (β-ket: β-ketiminate mono anion), have been synthesized from the reaction between [Ru(acac)$_2$(RCN)$_2$] (R = CH_3 or C_6H_5) [21–23] and ketones (Fig. 1). The similar procedure was used to synthesize all β-ketiminato complexes.

*3.3.3.1. [Ru(acac)$_2$(mhmk)] (**1**).* In a typical experiment, [Ru(acac)$_2$(AN)$_2$] (0.38 g; 1.0 mmol) was added to acetone (300 cm^3) and this mixture was stirred at 40 °C for 24 h. During the course of the reaction, the color of the solution turned from yellowish orange to violet. The solvent was then evaporated under vacuum and the residue was chromatographed on a silica gel column. A purple fraction that eluted with benzene–acetonitrile (4:1 v/v) was collected and it was again chromatographed. A pure purple fraction was eluted with benzene–acetonitrile (4:1 v/v). The solvent was evaporated to yield purple [Ru(acac)$_2$(mhmk)]. The formation of β-ketiminate has been supported by the appearance of a sharp band due to ν(N–H) at 3263 cm^{-1} in the FT-IR spectrum of complex **1**. However, we could not observe any signal due to the proton on the N atom in

its ^{1}H NMR spectrum. This may be due to fast exchange with deuterium. Purple crystals, Yield: 0.14 g (35% based on Ru). FAB-Mass: $m^+/z = 398$ (M^+). FT-IR Spectrum: ν(N–H) = 3263 cm^{-1}. *Anal.* Calc. for $C_{15}H_{22}NO_5Ru$ (397.41): C, 45.33; H, 5.58; N, 3.40. Found: C, 45.53; H, 5.82; N, 3.22%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -1.09$, -2.62, 1.7, 4.55 (each s, 3H, acac's β-CH_3), -29.5, -20.9 (each s, 3H, mhmk's β-CH_3), -6.76 (s, 1H, acac's γ-H), -22.1 (s, 1H, acac's γ-H), the γ-H of the β-ketiminate could not be observed.

*3.3.3.2. [Ru(acac)$_2$(ehmk)] (**2**).* The reaction was carried out by the same procedure as described for **1** with [Ru(acac)$_2$(AN)$_2$] (0.19 g; 0.5 mmol) in ethylmethyl ketone (100 cm^3) and stirred at 30 °C for 10 h. The color of the solution turned to violet. The residue was subjected to chromatographic separation as described for **1** and a reddish purple fraction containing **2** was obtained. Yield: 0.07 g (34% based on Ru). FAB-Mass: $m^+/z = 412$ (M^+). FT-IR: ν(N–H) = 3263 cm^{-1}. *Anal.* Calc. for $C_{16}H_{24}NO_5Ru$ (411.44): C, 46.71; H, 5.88; N, 3.40. Found: C, 46.86; H, 5.84; N, 3.34%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -6.31$, -5.96, 3.66, 5.70 (each s, 12H, acac's β-CH_3), 0.26, -29.7 (2H, methyne proton of acac) -19.45, -30.7 (each s, 2H, CH_2 of ehmk), 8.15 (s, 3H, *N*–CH_3 of ehmk), -22.4 (s, 3H, *O*–CH_3 of ehmk).

*3.3.3.3. [Ru(acac)$_2$(mAmk)] (**3**).* The reaction was carried out in a similar manner to that described for **2** with [Ru(acac)$_2$(AN)$_2$] (0.50 g; 1.3 mmol) in acetylacetone (100 cm^3). The color of the solution turned to violet. After the usual work up, the reddish-purple fraction obtained by chromatographic separation yielded **3**. Yield: 0.06 g (10% based on Ru) FAB-Mass: $m^+/z = 440$ (M^+). FT-IR: ν(Ac of mAmk C═O) = 1672 cm^{-1}, ν(N–H) = 3256 cm^{-1}. *Anal.* Calc. for $C_{17}H_{24}NO_6Ru$ (439.45): C, 46.46; H, 5.50; N, 3.19. Found: C, 46.20; H, 5.41; N, 3.16%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -3.98$, -3.06, 2.17, 3.78 (each s, 12H, acac's β-CH_3), -7.01, -26.4 (s, 2H, methyne proton of acac), 12.5 (s, 3H, γ-Ac–CH_3 of mAmk), -12.5 (s, 3H, *N*–CH_3 of mAmk), -28.2 (s, 3H, *O*–CH_3 of mAmk).

*3.3.3.4. [Ru(acac)$_2$(mClmk)] (**4**).* The reaction was carried out in a similar manner to that described for **2** with [Ru(acac)$_2$(AN)$_2$] (0.10 g; 0.26 mmol) in monochloroacetone (25 cm^3). The color of the solution turned to violet. After the usual work up, the green fraction obtained yielded purple crystals **4**. Yield: 0.01 g (9% based on Ru). FAB-Mass: $m^+z = 432$ (M^+). FT-IR: ν (N–H) = 3254 cm^{-1}. *Anal.* Calc. for $C_{15}H_{21}ClNO_5Ru$ (431.85): Calc: C, 52.28; H, 5.26; N, 3.05. Found: C, 52.61; H, 5.34; N, 2.92%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -2.80$, -2.04, 1.98, 3.74 (each s, 12H, acac's β-CH_3), -3.29, -23.4 (each s, 2H, methyne proton of mClmk), -19.2 (s, 3H, *N*–CH_3 of mClmk), -34.6 (s, 3H, *O*–CH_3 of mClmk).

*3.3.3.5. [Ru(acac)$_2$(mhbk)] (**5**).* The reaction was carried out by the same procedure as described for **1** with [Ru(acac)$_2$(BN)$_2$] (0.40 g; 0.87 mmol) in acetone (50 cm^3) and the solution was stirred at 30 °C for 24 h. The color of the solution turned to brown from orange. After the usual work up, the brown fraction containing **5** was obtained. Yield: 0.14 g (38% based on Ru). FAB-Mass: $m^+/z = 459$ (M^+). FT-IR: ν(N–H) = 3278 cm^{-1}. *Anal.* Calc. for $C_{20}H_{24}NO_5Ru$ (459.48): C, 52.28; H, 5.26; N, 3.05. Found: C, 52.61; H, 5.34; N, 2.92%. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = -1.82$, 0.02, 1.0, 2.01 (acac's β-CH_3), -15.2, -16.35 (2H, methyne proton of acac),-29.3(s, 3H, *O*–CH_3 of mhbk). 5.66, 5.67, 10.04, 10.09 (phenyl–H of bhmk).

*3.3.3.6. [Ru(acac)$_2$(ehbk)] (**6**).* The reaction was carried out in a similar manner to that described for **5** with [Ru(acac)$_2$(BN)$_2$] (0.40 g; 0.87 mmol) in ethyl methyl ketone (50 cm^3). After the usual work up, the brown fraction containing **6** was obtained. Yield: 0.11 g (25% based on Ru). FAB-Mass: $m^+/z = 473$ (M^+). FT-IR: ν(N–H) = 3280 cm^{-1}. *Anal* Calc. for $C_{21}H_{26}NO_5Ru$ (473.50): C, 53.27; H, 5.53; N, 2.96%. Found: C, 53.19; H, 5.44; N, 2.87%. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = -3.51$, -3.36, 2.84, 3.84 (each s, 12H, acac's β-CH_3), -6.71, -26.3 (s, 2H, methyne proton of acac), 5.59, 5.60, 10.32 (5H, phenyl–H of ehbk). -29.8, -20.3 (each s, 2H, CH_2 of ehbk), 4.63(s, 3H, *O*–CH_3 of ehbk).

4. Conclusion

Six novel compounds of β-ketiminato ruthenium complexes were synthesized from the reaction of coordinated organonitrile with bis(acetylacetonato)ruthenium(II) in ketones. The reaction mechanism was presumed to proceed as follows: the reaction started by the substitution of coordinated nitrile to ketone and then new carbon–carbon bonding was formed between the carbon in the nitrile and neighboring methylene carbon on the carbonyl group of ketone. The β-ketiminato complexes were oxidized and reduced with reversible one-electron transfer electrode processes corresponding to $Ru^{III} \rightarrow Ru^{IV}$ and $Ru^{III} \rightarrow Ru^{II}$, respectively. The reversible half-wave potentials ($E_{1/2}$) of the β-ketiminato complexes showed significant negative shifts in their reductions as well as their oxidations when compared to those of the corresponding β-diketonato complexes. The negative shifts are attributable to the differences of the electronegativity between the coordinated atoms O and N. The effects of the substituent in β-ketiminato complexes on the half-wave potential could be interpreted by the strength of electron donor

ability of substituents. Linear relationships were obtained between $E_{1/2}$ value and the Hammett constant of the substituents on β-ketiminate and the slopes of the lines of $E_{1/2}$ (ox) and $E_{1/2}$ (red) were nearly the same as those of β-diketonato and β-ketiminato complexes. From such results, it may be concluded that the six member ring consisting of ruthenium(III) and β-ketiminate is conjugated as well as that of ruthenium(III) and β-diketonate. The structures of the β-ketiminato complexes obtained here were very similar to those of β-diketonato complexes.

5. Supplementary material

Crystallographic data of complexes **2**–**6** (excluding structure factors) for the structures reported in this paper have been submitted to the Cambridge Crystallographic Data Centre (CCDC) as Supplementary Publication Nos. CCDC-242421–242425. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The ORTEP diagram and selected structure factors of complex **1** were reported in Ref. [11].

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