Reaction of Acetone on Coodinated Nitrile in β-Diketonato Ruthenium Complex, $[Ru(acac)_2(CH_3CN)_2]$ with the formation of β-Ketiminate

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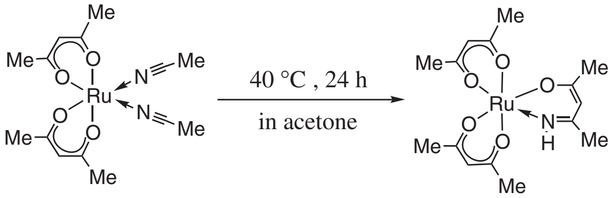
Synthesis and characterization of a new ruthenium complex, $[Ru(acac)_2(mhmk)]$ (**1**) with coordinated β-ketiminate ligand are described. The complex has been obtained by the reaction of acetone on coordinated acetonirile in $[Ru(acac)_2(CH_3CN)_2]$, the first such reaction to be observed. X-ray structure of **1** is similar to that of $[Ru(acac)_3]$. Cyclic voltammetric studies of **1** show a negative shift for both reduction and oxidation indicating that there is large electron density on ruthenium containing β-ketiminate ligand when compared to ruthenium containing only β-diketonato ligands, $[Ru(acac)_3]$.

A great deal of work has been done on the coordinated nitrile ligands in transition metal complexes which lead to their conversion into other organic compounds due to chemical reactions like insertion, coupling, and electrophilic or nucleophilic attack.[1] Very 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 found to be enhanced by coordination of nitriles to various metal centers.[3] Though vinylimido complexes react with unsaturated organic species allowing cross coupling of nitriles with ketones affording new carbon–carbon bonded compounds, no such reaction of acetone on coordinated nitrile ligand has been shown to give such compounds.[4] Nakamura et al. have reported the formation of β-ketoamine 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.[5] However, to our knowledge there is no report of the reaction of acetone on coordinated nitrile ligand leading to the fomation of β-ketiminate. Hence, we report in this letter the reaction of acetone on the coordinated nitrile in a β-diketonato ruthenium complex with the formation of β-ketiminate. This reaction, besides being novel, is not only the first report of the reaction of acetone on the coordinated nitrile ligand but also is a new and simple method for the formation β-ketimine on ruthenium ion. Generally, simple β-ketimine with no substitution on N atom is very unstable and only alkyl or aryl substituted β-ketimines are known.

Though there are several reports on the nucleophilic attack on coordinated nitriles in transition metal complexes, no such reaction has so far been known to have taken place with acetone. During the course of our systematic investigations on the reactions of β-diketonato ruthenium complexes containing acetonitrile, we have found that acetone attacks coordinated acetonitrile in ruthenium complex, $[Ru(acac)_2(CH_3CN)_2]$ leading to the formation of β-ketiminate on ruthenium ion. This nucleophilic attack is not only surprising so far as acetone is concerned but also demonstrates a new route to the formation of β-ketimine, a very unstable species in its simple form. To our knowledge, this is probably the first report of the reaction of acetone on coordinated nitriles in a metal complex.

The complex $[Ru(acac)_2(mhmk)]$ (**1**) has been synthesized from $[Ru(acac)_2(CH_3CN)_2]$[6] and acetone (Scheme 1). In a typical experiment, $[Ru(acac)_2(CH_3CN)_2]$ (0.380 g; 0.1 mmol) was added to acetone (300 cm^3) and stirred at 40 °C for 24 h. During the course of the reaction, the color of the solution turned to violet from yellowish orange. The solvent was then evaporated under vacuum and the residue was chromatographed on silica gel column. A purple fraction 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 $[Ru(acac)_2(mhmk)]$.[7] Yield: 0.14 g (35% based on Ru).



$[Ru(acac)_2(AN)_2]$ $[Ru(acac)_2(mhmk)]$

Scheme 1.

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 **1**. However, we could not observe any signal due to the proton on N atom in its ^1H NMR spectrum. This may be due to fast exchange with deuterium.

The structure of **1** has been determined by single crystal X-ray diffraction. The crystal and molecular structure and the important bond lengths and bond angles are given in Figure 1.[8] The structure can be described as distorted octahedron with mhmk ligand and ruthenium atom in one plane. The general structural features are very similar to the that of $[Ru(acac)_3]$.[9] The Ru–O lengths observed for acac and that of β-ketiminate are almost the same. However, the Ru–N distance is little shorter and this 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 observed in a rhodium ketiminate complex.[11]

The cyclic voltammograms of **1** and $[Ru(acac)_3]$ are shown in Figure 2. One reduction and one oxidation peaks were observed for both the complexes. $[Ru(acac)_3]$ showed one reduc-

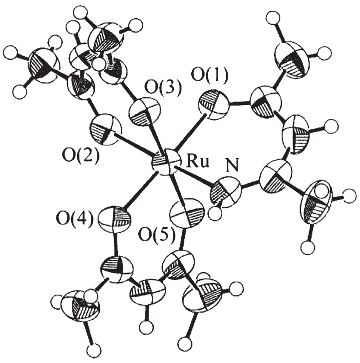


Figure 1. Molecular structure of [Ru(acac)$_2$(mhmk)] (**1**). Selected bond lengths (Å) and angles (°): Ru–O(1) = 1.996(3), Ru–O(2) = 2.056(3), Ru–O(3) = 2.030(3), Ru–O(4) = 2.032(3), Ru–O(5) = 2.013(3), Ru–N = 1.976(3); O(1)–Ru–O(4) = 176.8(1), O(3)–Ru–O(5) = 179.2(1), O(2)–Ru–N = 178.5(1), O(2)–Ru–O(3) = 90.6(1), O(4)–Ru–O(5) = 91.4(1), O(1)–Ru–N = 93.0(1).

tion wave at $E_{1/2} = -1.17$ V and an oxidation wave at $E_{1/2} = 0.60$ V. The complex **1** showed a reduction wave at $E_{1/2} = -1.34$ V and an oxidation wave at $E_{1/2} = 0.37$ V. The peak potentials were independent of the sweep rate, suggesting that the waves are Nernstian one electron processes. The complex **1** showed a significant negative shift in its reduction (0.17 V) as well as its oxidation (0.23 V) when compared to that of [Ru(acac)$_3$]. The large negative shifts are due 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 O atom and hence, there may be more electron density on ruthenium containing β-ketiminate ligand compared to acetylacetonate ligand. This is probably the reason for the large negative shifts in potentials for the reduction (Ru^{III}–Ru^{II}) and oxidation (Ru^{III}–Ru^{IV}). In other words, the ring consisting of ruthenium and β-ketiminate (O^N) has larger electron density than the ring consisting of ruthenium and acetylacetyonate (O^O).

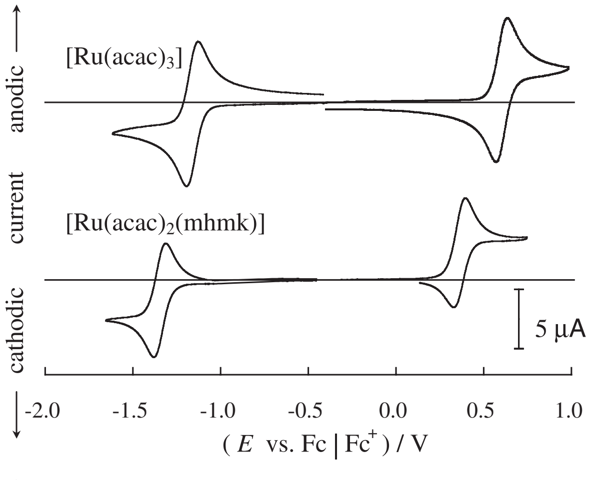


Figure 2. Cyclic voltammograms of complexes in acetonitrile solution containing 0.1 mol dm^{-3} tetraethylammonium perchlorate at 25 °C. The test electrode is a stationary platinum disk ($\phi = 1.6$ mm). The potentials are measured against Ag | AgCl (3 mol dm^{-3} NaCl aq. solution). The concentrations of complexes are 1 mmol dm^{-3} and the potential scan rate is 0.1 V s^{-1}.

References and Notes

1 R. A. Michelin, M. Mozzon, and R. Bertini, *Coord. Chem. Rev.*, **147**, 299 (1996).

2 H. Nagao, T. Hirano, N. Tsuboya, S. Shiota, M. Mukaida, T. Oi, and M. Yamasaki, *Inorg. Chem.*, **41**, 6267 (2002), and references cited therein.

3 H. Nagao, K. Ito, N. Tsuboya, D. Ooyama, N. Nagao, F. S. Howell, and M. Mukaida, *Inorg. Chim. Acta*, **290**, 113 (1999); I. I. Creaser, J. M. B. Horrowfield, F. R. Keene, and A. M. Sargeson, *J. Am. Chem. Soc.*, **103**, 3559 (1981); P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, **1998**, 2373; P. Chollhammer, M. L. Henanf, C. L. R. L. Floch, F. Y. Petillon, J. Talarmin, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, **2001**, 1573; H.-Y. Huang, W.-J. Chen, C.-C. Yang, and A. Yeh, *Inorg. Chem.*, **30**, 1862 (1991); A. W. Zanella and P. C. Ford, *Inorg. Chem.*, **14**, 42 (1975); C.-S. Chin, D. Chong, B. Lee H. Jeong, G. Won, Y. Do, and Y. J. Park, *Organometallics*, **19**, 4043 (2000); N. V. Kaminskaia, I. A. Guzei, and N. M. Kostic, *J. Chem. Soc., Dalton Trans.*, **1998**, 3879; W.-Y. Yeh, S.-M. Peng, and L.-K. Liu, *Inorg. Chem.*, **32**, 2965 (1993).

4 K. M. Doxsee, J. B. Farahi, and H. Hope, *J. Chem. Soc., Chem. Commun.*, **1990**, 1452; K. M. Doxsee, J. B. Farahi, and H. Hope, *J. Am. Chem. Soc.*, **113**, 8889 (1991).

5 T. Uchiyama, K. Takagi, K. Matsumoto, S. Ooi, Y. Nakamura, and S. Kawaguchi, *Chem. Lett.*, **1979**, 1197; T. Uchiyama, K. Takagi, K. Matsumoto, S. Ooi, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1077 (1981); Z. Kanda, Y. Nakamura, and S. Kawaguchi, *Inorg. Chem.*, **17**, 910 (1978).

6 Y. Kasahara, Y. Hoshino, K. Shimizu, and G. P. Satô, *Chem. Lett.*, **1990**, 381.

7 FAB-Mass: $m/z = 398$ (M^+). FT-IR: ν (N–H) = 3263 cm^{-1}. Anal. Found; C, 45.53, H, 5.82, N, 3.22%, Calcd; C, 45.33, H, 5.58, N, 3.52%. ^{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 obseved.

8 Crystal and analytical data for [Ru(acac)$_2$(mhmk)], $C_{15}H_{22}NO_5Ru$; fw = 397.41; Monoclinic, C_2/c (#15), $Z = 8$, $a = 18.780(1)$ Å, $b = 12.9842(7)$ Å, $c = 15.765(1)$ Å, $\beta = 115.023(2)°$, $V = 3483.4(4)$ Å^3, $D_{\mathrm{calcd}} = 1.515$ g cm^{-1}, μ(Mo Kα) = 9.21 cm^{-1}, Final $R = 0.064$ ($R_w = 0.131$) for 3966 observed reflections. Measurements for diffraction data were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer. The structures were solved by direct methods and refined by a full-matrix least-squares treatment. The position of proton on nitrogen atom was calculated from the phenyl proton.

9 G.-K.-J. Chao, R. L. Sime, and R. J. Sime, *Acta Crystallogr.*, **B29**, 2845 (1973).

10 C. F. Works, C. J. Jocher, G. W. Bart, X. Bu, and P. C. Ford, *Inorg. Chem.*, **41**, 3728 (2002).

11 J. L. Demoense, W. Purcell, A. Roodt, and G. J. Leipoldt, *Rhodium Express*, **5**, 10 (1994).

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