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Epoxidation activities of mononuclear ruthenium–oxo complexes with a square planar 6,6′-bis(benzoylamino)-2,2′-bipyridine and axial ligands

Koichiro Jitsukawa,* Hiroyoshi Shiozaki and Hideki Masuda

Department of Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan

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Abstract—Some ruthenium complexes, [Ru^{II}(babp)(dmso)(L)], with a square planar ligand, H_2BABP, and axial ligands, L (L = dmso, imidazole, or pyridine derivatives), have been prepared as catalysts for oxygen-transfer reactions. The catalytic activity and selectivity of the metal–oxo species derived from these complexes and PhIO have been affected by the axial ligands L, in which active species has been interpreted in terms of contribution of both characters of Ru(V)=O and Ru(IV)–O·. © 2002 Elsevier Science Ltd. All rights reserved.

In various oxidation processes using metal porphyrins and oxygen donors, some high valent metal–oxo species are considered as the active intermediates.[1] The high valent iron–oxo intermediates in the enzyme reactions catalyzed by hemeproteins play an important role for oxidative transformation of bio-related compounds.[2] However, such Fe=O species have not been fully characterized because of their labilities. Therefore, the Ru=O species, which is the oxo complexes of the stable homologous element and is often utilized in the place of iron, have been investigated by a combination with porphyrin or polypyridine ligands.[3] Ru(IV, V, or VI)–oxo species, generated through the reaction of low valent Ru(II or III) complexes and various oxidants, are widely utilized as the catalysts of oxygen-transfer reactions,[4] in which iodosobenzene (PhIO) is sometimes employed as an efficient two-electron oxidant for such ruthenium-catalyzed oxidations in order to avoid the complicated oxidation pathway due to the peracid itself.[3,4] Recently, we have reported that ruthenium complexes with tripodal tris(2-pyridylmethyl)amine derivatives catalyze hydroxylation of adamantane and epoxidation of cyclohexene with assistance of PhIO, in which the oxidation activity has been affected by the electronic and steric character of the oxo species.[5] The tripodal polypyridine derivatives, however, are not sufficient ligands for understanding the character of the Ru=O species, because the bulky pivalamido groups around metal center sterically suppress the reactions and the α-hydrogen of the pyridine group is often hydroxylated in the course of reaction.[5,6] Hence, taking account of the *trans*-influence that the catalytic activity in cytochrome P-450 is affected by the axially-coordinated proximal ligand in the position *trans* to metal–oxo,[7] the molecular design of a square-planar aromatic ligand is required for controlling the oxidation activity of the axial metal–oxo site by another axial ligand. Here, a tetradentate square-planar ligand, 6,6′-bis(benzoylamino)-2,2′-bipyridine (H_2BABP), which is expected to resist the oxidative degradation, is employed for this purpose.[8] Some ruthenium complexes with monodentate heterocyclic compounds as axial ligands were prepared and their catalytic activity for oxygen-transfer reaction were examined.

The ruthenium complexes here employed were prepared and characterized as follows: [Ru^{II}(babp)(dmso)$_2$] (**1**), was obtained as an orange crystal from the reaction of *cis*-[RuCl$_2$(dmso)$_4$][9] and H_2BABP in the presence of NaH in DMF solution. Addition of equimolar amount of heterocyclic compounds (imidazole (Im), pyridine (Py), 4-phenylpyridine (Phpy), and 4-methylpyridine (Mepy)) to the DMSO solution of **1** gave the corresponding complexes, [Ru^{II}(babp)(dmso)(im)] (**2**), [Ru^{II}(babp)(dmso)(py)] (**3**), [Ru^{II}(babp)(dmso)(phpy)] (**4**), and [Ru^{II}(babp)(dmso)(mepy)] (**5**), respectively. Characterization of these complexes were performed by ^{1}H NMR spectroscopy and the elemental analyses.[10] The crystal structure of **5**, which was fortunately obtained as a single crystal suitable for X-ray analysis,

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* Corresponding author. E-mail: jitkk@ach.nitech.ac.jp

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revealed that the ruthenium center was 4-coordinated with the deprotonated BABP as a dianion in a square planar geometry and with monodentate 4-methylpyridine and dimethyl sulfoxide at the two axial positions, as shown in Fig. 1. The redox potentials (Ru(II/III)) of these complexes, which were measured in CH_3CN solution by cyclic voltammetry, indicated the ligand effect as shown in Fig. 2. The ruthenium complex with imidazole ligand (**2**) showed lower redox potential value in comparison with that with two dmso molecules (**1**), while those with the pyridine derivatives (**3**–**5**) showed higher values. This finding indicates that the complex **2** stabilizes the higher oxidation state and the latter complexes **3**–**5** do the lower oxidation state.

Oxidation of olefins catalyzed by the ruthenium complexes **1**–**4** has been carried out at 40°C for 4 h under Ar atmosphere in the presence of PhIO (Ru:olefin:PhIO = 1:100:100). Epoxidation of *cis*-stilbene by **1** or **2** gave the corresponding epoxide accompanied by small amount of *trans*-epoxide and much amount of C=C bond cleavage product, benzaldehyde, as listed in Table 1. Such a reactivity has been also reported by Katsuki et al.; Ru(III)–salen complexes gave epoxide in poor yield in comparison with those by the corresponding Mn(III) complexes.[11] In the cases of **3** and **4** containing pyridine derivative as an axial ligand, significant decrease in the yield of stilbene oxide and increase in that of benzaldehyde were demonstrated. These ruthenium complexes showed similar reactivity for the oxidation of *trans*-stilbene as well as the cases of *cis*-stilbene. These findings are comparable to the previous report that the epoxidation of *trans*-stilbene by the combined system of $RuCl_3$, $NaIO_4$, and chiral bis(dihydrooxazolylphenyl)oxalamide ligand in CH_2Cl_2 solution gave epoxide in a 31% yield accompanied with significant amount of benzaldehyde.[12]

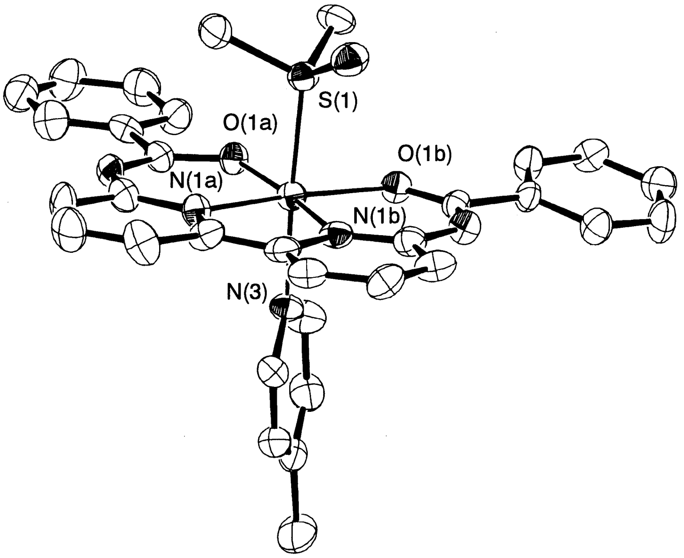


Figure 1. ORTEP drawing of [Ru(babp)(dmso)(mepy)] complex (**5**). Typical bond lengths (Å) and angles (°): Ru–N(3) 2.132(8), Ru–S(1) 2.239(3), Ru–N(1a) 1.987(9), Ru–N(1b) 1.992(9), Ru–O(1a) 2.082(7), Ru–O(1b) 2.071(7); S(1)–Ru–N(3) 174.9(2), N(1a)–Ru–N(1b) 81.3(4), N(1a)–Ru–O(1a) 92.8(3), N(1a)–Ru–O(1b) 173.2(3).

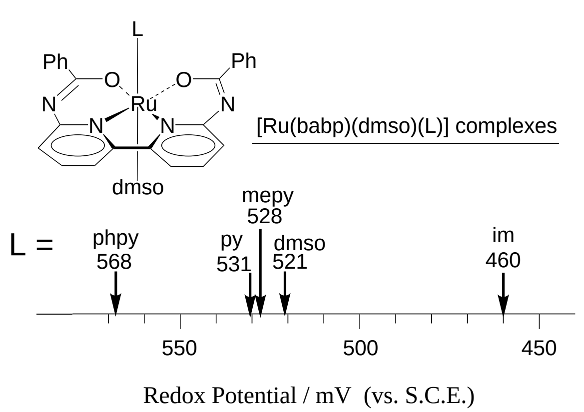
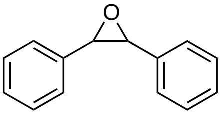
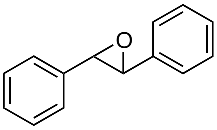
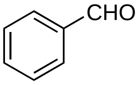


Figure 2. Redox potential values of ruthenium complexes, [Ru(babp)(dmso)(L)].

Epoxidation activity for *cis*-cyclooctene has been examined under the same conditions as above. The yields of cyclooctene oxide decreased in the order of **2** (30%)>**1** (24%)>**3** (13%)>**4** (4.2%), which was the same as the case of stilbene oxidation. Such a decrease in the yield significantly correlates to the order of redox potentials of the complexes, implying that the catalytic activity of the Ru complexes here employed depends on their axial ligands. Generally, epoxidation of *cis*-cyclooctene catalyzed by ruthenium complexes did not proceed quantitatively; for example, cyclooctene oxide was obtained in a 19% yield when the other mononuclear ruthenium(III) complex with Schiff base ligand was used.[13] Oxidation of cyclohexene catalyzed by **1**–**4** has also been carried out and the results are summarized in Table 2. It is well known that oxidation of cyclohexene initiated by the metal–oxo species under anaerobic condition gives cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, where the first compound is obtained through epoxidation and the latter two are derived from allylic oxidation. The ratio of the epoxidation product yield to the allylic oxidation ones was almost constant during the initial stage of the reaction catalyzed by these ruthenium complexes. Notably, catalytic activity of **2** for epoxidation was superior to those of **3** and **4** as well as indicated in the case of other olefins. On the other hand, allylic oxidation products were formed in almost equal amounts for **1**–**4**. In the oxidation of *cis*-cyclooctene without active allylic methylene protons,[14] only the electrophilicity of the catalytic species might control the reactivity, while in the case of cyclohexene, the substrate has alternative reaction points for making an estimate of the reactivity of the metal–oxo species. We consider that oxidation pathways catalyzed by the ruthenium–oxo species for epoxidation and allylic oxidation might proceed through different intermediates to each other. Probably, epoxidation favors higher oxidation state of the metal–oxo species.

According to the Meyer's discussion that Ru(IV)=O species prefers attack on the C–H bond to that on the

Table 1. Oxidation of *cis*- and *trans*-stilbenes catalyzed by Ru–babp complexes[a]

Complexes	Yield (%)[b]		
			
		cis-Stilbene	
[Ru(babp)(dmso)(im)] (**2**)	28	2.3	32
[Ru(babp)$(dmso)_2$] (**1**)	20	2.2	48
[Ru(babp)(dmso)(py)] (**3**)	7.8	1.3	50
[Ru(babp)(dmso)(phpy)] (**4**)	6.6	1.4	53
		trans-Stilbene	
[Ru(babp)(dmso)(im)] (**2**)	Not detected	28	28
[Ru(babp)$(dmso)_2$] (**1**)	Not detected	19	34
[Ru(babp)(dmso)(py)] (**3**)	Not detected	14	44
[Ru(babp)(dmso)(phpy)] (**4**)	Not detected	12	45

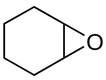
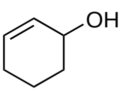
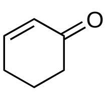
[a] Catalyst, 1 mM; substrate 100 mM; PhIO 100 mM; 1,2-dichloroethane, 40°C, 4 h.

[b] GC yield based on the substrate.

olefinic double bond,[15] the complex **2**, exhibiting epoxidation activity rather than allylic oxidation one, might proceed through the reaction intermediate higher than the Ru(IV) state.[4] Fortunately, the formation of high valent Ru=O species has been demonstrated by positive-ion ESI mass spectroscopy: The reaction of **1** and 10 equiv. of PhIO in dichloromethane showed prominent peak clusters at *m*/*z* 494.0 and 510.2, corresponding to the $[Ru^{III}(babp)]^+$ and $[Ru^{V}(babp)(O)]^+$ ions, respectively (Fig. 3).[16] The latter was not detected with addition of olefins. These results indicate that the catalytic species of the ruthenium complexes might be a mononuclear Ru(V)=O generated through the two-electron oxidation process by PhIO, e.g. Ru(III)/Ru(V) redox couple, where the Ru(III) species could be generated through comproportionation between the starting Ru(II) complex and the Ru(IV) species oxidized by PhIO. The redox potentials of **1**–**4** (Fig. 2) reveal that the complex **2** could stabilize the higher oxidation state compared with **1**, **3** and **4**, so that the electrophilicity of the metal–oxo species in **2** is superior to those of **1**, **3** and **4**. On account for the accompanying reactions, allylic oxidation and C=C bond cleavage reaction, radical character is presumed as a reaction intermediate. We consider that this oxygen-transfer reaction catalyzed by the ruthenium complex with a square planar ligand might proceed through the reaction intermediate having a combination of oxo and radical characters in the transition state, although various mechanistic investigations have been reported on the ruthenium–oxo complexes.[3,15] The ruthenium complex **2** with imidazole as an axial ligand exhibiting lower redox potential value might induce the higher oxidation intermediate such as Ru(V)=O species, while the pyridine derivatives, **3** and **4**, preferentially afford the lower one, Ru(IV)–O·.

In summary, the oxygen-transfer reaction catalyzed by the high valent ruthenium complexes with a square planar geometry and PhIO have been examined. The catalytic intermediate species might be demonstrated in terms of contribution of both characters of Ru(V)=O and Ru(IV)–O·, which are controlled by the axial ligand of the complexes.

Table 2. Oxidation of cyclohexene catalyzed by Ru–babp complexes[a]

Complexes	Yield (%)[b]		
	Epoxidation	Allylic oxidation	
			
[Ru(babp)(dmso)(im)] (**2**)	22	0.8	5.3
[Ru(babp)$(dmso)_2$] (**1**)	19	0.4	5.2
[Ru(babp)(dmso)(py)] (**3**)	10	0.5	6.8
[Ru(babp)(dmso)(phpy)] (**4**)	7.5	0.7	7.9

[a] Catalyst, 1 mM; substrate 100 mM; PhIO 100 mM; 1,2-dichloroethane, 40°C, 4 h.

[b] GC yield based on the substrate.

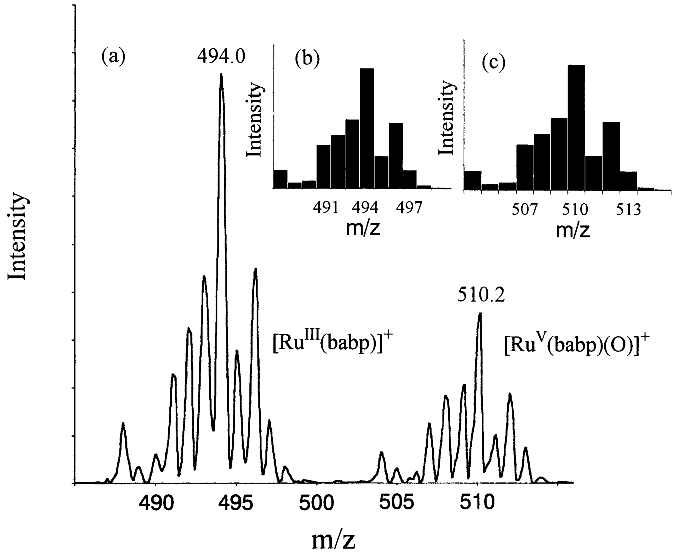


Figure 3. (a) Positive-ion ESI mass spectrum of the intermediate species generated from the reaction of $[Ru^{II}(babp)(dmso)_2]$ (**1**) and PhIO. (b) Simulation pattern for $[Ru^{III}(babp)]^+$. (c) Simulation pattern for $[Ru^V(babp)(O)]^+$.

Acknowledgements

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