



Reverse reactivity in hydroxylation of adamantane and epoxidation of cyclohexene catalyzed by the mononuclear ruthenium-oxo complexes with 6-substituted tripodal polypyridine ligands

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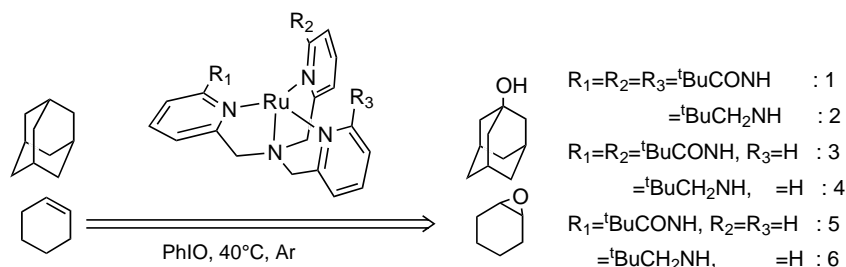
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Abstract—The electronic character of the ruthenium complexes with tripodal polypyridine ligands, which is controlled by the substituted groups at pyridine 6-position, gives rise to differences in the reactivity for the ruthenium catalyzed hydroxylation of adamantane and epoxidation of cyclohexene with PhIO as an oxidant; Ru complexes containing electron-withdrawing groups (**1**, **3**, and **5**) promote the epoxidation, while those containing electron-donating groups (**2**, **4**, and **6**) promote the hydroxylation. © 2001 Elsevier Science Ltd. All rights reserved.

High valent metal-oxo species have been considered as active intermediates in various oxidation processes catalyzed by transition metal complexes.¹ Ruthenium-oxo species generated through the reactions of low valent ruthenium complexes and various oxidants are widely utilized as catalysts of oxygen transfer reactions.² In previous work, tetradentate tripodal polypyridine ligands were used to prepare the ruthenium complexes.³ We have also investigated the stability/reactivity of superoxide and peroxide species combined with the transition metal complexes with tripodal polypyridine ligands, in which hydrogen bonds, steric effects and electronic effects have been shown to be crucial factors.⁴ Recent reports have described that ruthenium complexes with the tris(2-pyridylmethyl)amine (TPA) ligand catalyzed the hydroxylation and epoxidation of organic compounds in the presence of MCPBA (*m*-

chloroperbenzoic acid) through the putative Ru=O species.⁵ Evidence for the high valent Ru species on the above reactions has not yet been confirmed. Further complications are caused by the fact that MCPBA itself is capable of the hydroxylation of adamantane and promotion of the Baeyer–Villiger reaction of ketones. Here, using PhIO (iodosobenzene), an efficient 2-electron oxidant for ruthenium catalyzed oxidations,^{2,6} we have investigated the catalytic reactivity of ruthenium complexes with tripodal ligands for hydroxylation of adamantane and epoxidation of cyclohexene.

The tripodal polypyridine ligands, tppa, bppa, mppa, tnpa, bnpa and mnpa were synthesized according to the methods previously reported.⁴ Tppa, bppa and mppa have electron-withdrawing character, while tnpa, bnpa and mnpa are electron-donating. The ruthenium com-



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plexes, $[\text{Ru}^{\text{II}}(\text{tpa})\text{Cl}](\text{PF}_6)$ (**1**), $[\text{Ru}^{\text{III}}(\text{tnpa})\text{Cl}_2](\text{PF}_6)$ (**2**), $[\text{Ru}^{\text{II}}(\text{bppa})\text{Cl}](\text{PF}_6)$ (**3**), $[\text{Ru}^{\text{III}}(\text{bnpa})\text{Cl}_2](\text{PF}_6)$ (**4**), $[\text{Ru}^{\text{II}}(\text{mppa})\text{Cl}](\text{PF}_6)$ (**5**) and $[\text{Ru}^{\text{III}}(\text{mnpa})\text{Cl}_2](\text{PF}_6)$ (**6**), were prepared and crystallized according to the method for $[\text{Ru}^{\text{II}}(\text{tpa})\text{Cl}_2](\text{ClO}_4)_2$.^{7,8} Oxidation of adamantane (68 mg, 0.5 mmol) in 1,2-dichloroethane solution (5 mL) was carried out at 40°C in the presence of PhIO (110 mg, 0.5 mmol) and a catalytic amount of ruthenium complex (0.005 mmol) under an Ar atmosphere. 1-Adamantanol was produced in moderate yield by **4**, but obtained in poor yield in the case of **3** as shown in Fig. 1. The yields of 1-adamantanol, a major hydroxylation product, were 3.9% in **1**, 12.1% in **2**, 4.9% in **3**, 11.8% in **4**, 3.5% in **5** and 12.0% in **6**, respectively, at the initial stage (4 h) of the reactions. The catalytic activities of the ruthenium complexes containing electron-withdrawing 6-pivalamide groups (**1**, **3**, and **5**)⁹ were relatively low in comparison with those containing electron-donating 6-neopentyl groups (**2**, **4**, and **6**). This finding clearly indicates a correlation with the redox properties of the complexes.¹⁰

The epoxidation activities catalyzed by these complexes were also affected by the substituent groups of the ligands. Complex **3** efficiently epoxidized cyclohexene under the same conditions as the hydroxylation of adamantane, as shown in Fig. 2. After 4 h, 46% of cyclohexene oxide and small amounts of allylic oxidation products, 2-cyclohexen-1-ol and 2-cyclohexen-1-one, were obtained. On the other hand, the reaction catalyzed by complex **4** gave 20% of cyclohexene oxide. This is in contrast to the above hydroxylation, in which the oxidation rate catalyzed by the complex **4** is faster than that by **3**. Reasons for such conflicting results obtained for hydroxylation and epoxidation are not yet clear. According to Meyer's argument, in which the $\text{Ru}(\text{IV})=\text{O}$ species prefers an attack on the C–H bond rather than the olefin double bond,¹¹ the ruthenium complexes **2**, **4** and **6** have the $\text{Ru}(\text{IV})=\text{O}$ character in the presence of PhIO. Notably, the complexes **1**, **3**, and **5** exhibit epoxidation activity rather than hydroxylation,

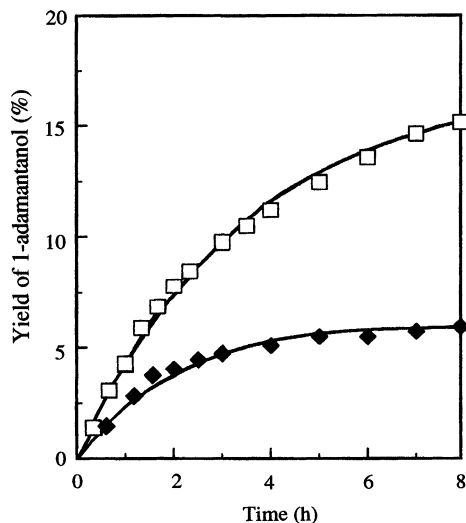


Fig. 1. Formation rates for 1-adamantanol in the oxidation of adamantane catalyzed by the complexes **3** (◆) and **4** (□).

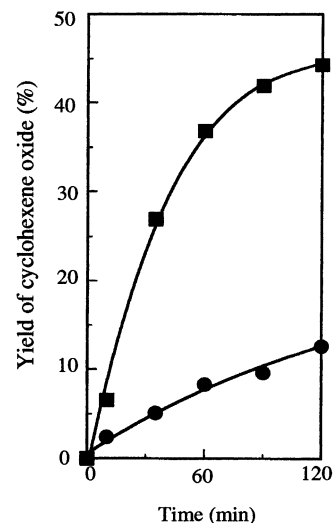


Fig. 2. Formation rates for cyclohexene oxide in the oxidation of cyclohexene catalyzed by the complexes **3** (■) and **4** (●).

tion, which suggests that the reaction intermediate is in an oxidation state higher than $\text{Ru}(\text{IV})$.² A positive ESI-mass spectrum of the reaction intermediate generated from **3** and 10 equiv. of PhIO in dichloromethane showed prominent peak clusters at m/z 624.2 and 640.2, corresponding to the $[\text{Ru}^{\text{III}}(\text{bppa}^-)\text{Cl}]^+$ and $[\text{Ru}^{\text{V}}(\text{bppa}^-)(\text{O})\text{Cl}]^+$ ions, respectively (Fig. 3). These results indicate that the catalytic species of the ruthenium complexes containing electron-withdrawing groups for epoxidation might be high valent mononuclear $\text{Ru}(\text{V})=\text{O}$ intermediates generated through the two electron process with PhIO, e.g. $\text{Ru}(\text{III})/\text{Ru}(\text{V})$ redox couple. The $\text{Ru}(\text{III})$ species from **3** could be generated through disproportionation of the starting $\text{Ru}(\text{II})$ complex and the $\text{Ru}(\text{IV})$ species oxidized by PhIO.

In conclusion, the catalytic activities of the ruthenium complexes for the hydroxylation of alkanes and the epoxidation of olefins in the presence of a 2-electron

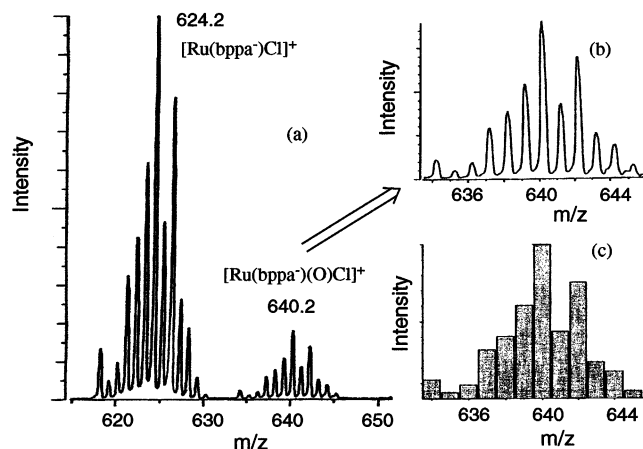


Fig. 3. (a) Positive-ion ESI-mass spectrum of the intermediate species generated from $[\text{Ru}^{\text{II}}(\text{bppa}^-)\text{Cl}](\text{PF}_6)$ (**3**) and PhIO. (b) Magnification of the parent peak clusters of the $[\text{Ru}(\text{bppa}^-)(\text{O})\text{Cl}]^+$ region. (c) Simulation pattern for $[\text{Ru}(\text{bppa}^-)(\text{O})\text{Cl}]^+$.

co-oxidant can be fine-tuned by the use of tripodal polypyridine ligands containing different substituent groups at the pyridine 6-position.

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- Abbreviations: tris(6-pivalamido-2-pyridylmethyl)amine, TPPA; tris(6-neopentyl-amino-2-pyridylmethyl)amine, TNPA; bis(6-pivalamido-2-pyridylmethyl)(2-pyridylmethyl)-amine, BPPA; bis(6-neopentylamino-2-pyridylmethyl)(2-pyridylmethyl)amine, BNPA; (6-pivalamido-2-pyridyl-methyl)bis(2-pyridylmethyl)amine, MPPA; and (6-neopentyl-amino-2-pyridylmethyl)-bis(2-pyridyl-methyl)-amine, MNPA.
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- Redox potentials (Ru(II/III), $E_{1/2}$ values measured in the cyclic voltammograms in CH₃CN solution with 0.1 M (*n*-Bu₄N)BF₄ as supporting electrolyte), were +0.558 V in **1**, +0.725 V in **3**, and +0.330 V in **5** (vs SCE), respectively, which were relatively higher than those of the corresponding complexes; +0.213 V in **2**, +0.203 V in **4**, and +0.210 V in **6** (Ru(III/II), vs SCE), respectively.
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