Catalytic Hydrocarbon Oxygenation by a Dinuclear Ruthenium(II) Complex with Molecular Oxygen

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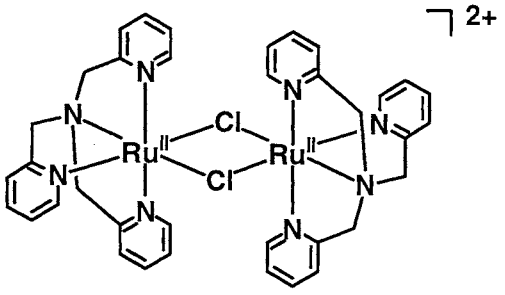
A bis-μ-chloro Ru(II) dimer with tris(2-pyridylmethyl)amine (TPA) exhibited catalytic oxygenation of alkenes and cooxygenation of alkanes in the presence of cyclohexene with molecular oxygen (1atm) at room temperature without reducing reagents; reactions proceeded via a radical chain mechanism as a main pathway.

Oxygenation of hydrocarbons with molecular oxygen is one of the most indispensable processes in metabolism of harmful organic compounds and production of biologically significant materials as functioning in biological systems. In many cases, they require metalloenzymes containing a metal ion as an active site.[1] The essential function of the metal center is dioxygen activation toward formation of active species, such as high-valent metal-oxo or metal-peroxo species. For example, heme enzymes such as cytochrome P-450's and non-heme enzymes such as methane monooxygenase involve Fe-porphyrins and dinuclear non-porphyrin Fe complexes as active sites, respectively.[2-4] Besides those biological systems, oxygenation reactions with molecular oxygen is also important for industrial production of many valuable materials from cheap and abundant natural resources as seen in the Wacker process for the production of acetaldehyde and Mid-Century process for that of telephthalic acid.[1]

On the other hand, as functional models for those enzymatic systems mentioned above, ruthenium complexes having a variety of ligands have contributed to gaining mechanistic insights into hydrocarbon functionalization.[5] In contrast to iron complexes as models, ruthenium complexes have been reported to be able to utilize dioxygen as an oxygen source to epoxidize olefins as observed in $Ru^{II}(TPP)/O_2$ (TPP = tetraphenyl porphyrin)[6] and $Ru^{II}(dmp)_2/O_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline) systems,[7] in both of which no reducing reagents are required. Ruthenium complexes can also activate peroxides such as H_2O_2,[7] *t*-butyl hydroperoxide (TBHP),[8] and pyridine-N-oxides[9] toward alkane functionalization. Recently, a Ru-substituted polyoxometalate has been reported to catalyse alkane hydroxylation by using molecular oxygen, however the reaction mechanism is still ambiguous.[10]



Along this line, we have investigated on ruthenium complexes having tripodal tetradentate pyridylamine ligand TPA as model compound to understand oxidation mechanism for ruthenium-catalyzed hydrocarbon functionalization. We have revealed that $[Ru^{III}Cl_2(TPA)]^+$ can catalyze alkane functionalization with use of mCPBA (*m*-chloroperbenzoic acid).[11] In this paper, we will describe hydrocarbon oxygenation with dioxygen in the presence of a bis-μ-chloro ruthenium(II) dimer, $[RuCl(TPA)]_2^{2+}$ (**1**),[12] as a catalyst without reducing reagents.

Reactions were performed in CH_3CN under O_2 (1 atm) including $1.0X10^{-5}$ mol of $\mathbf{1}\cdot(ClO_4)_2\cdot 1/2CH_3CN$ and 1000eq of substrate at room temperature. The reaction mixture was analyzed by GC with appropriate internal standards.

Product distributions are summarized in Table 1 with yields relative to the dimer. In the case of cyclohexene as a substrate,

Table 1. Catalytic oxygenation toward various substrates by **1** with dioxygen (1 atm) in CH_3CN at room temperature for 168 h

Substrate	Products (yield (%) based on catalyst)			
	OH (6100)	O (8500)	O (880)	
+ Me_2S	OH (7600)	O (3300)	O (0)	Me_2SO (2200)
a	O (240)			
a	OH (10200)	O (14900)	O (1900)	
	OH (700)	O (470)		

[a]Reaction time was 186 h.

allylic oxygenation was found to be main pathway and epoxidation as a minor reaction. In the absence of the complex, were obtained small amount of the alcohol and ketone (6-times more than alcohol) but no epoxide; 1/100 amount of cyclohexen-1-ol and 1/7 amount of cyclohexen-1-one were obtained relative to the reaction under catalytic conditions. These results suggest that the reactions are not due to merely free radical autoxidation but ruthenium species should be involved in the course of substrate oxygenation as mentioned below.

To expand the availability of this catalytic oxygenation by **1** with dioxygen, other substrates were examined as shown in Table 1. Cyclopentene was also epoxidized in comparable yield of 620% to that of cyclohexene (other products were not quantified). Norbornene was epoxidized but the yield was very poor compared with that of cyclohexene, owing to the difficulty of the formation of allyl radical of nobornene compared with cyclohexene because of steric effects. As for alkanes, cyclohexane was not oxidized as expected from observations mentioned so far, that is, allyl radical formation should be indispensable for the initiation of all the reactions; however, cyclohexane was oxygenated to give cyclohexanol and cyclohexanone in the presence of cyclohexene as co-substrate.[13] When adamantane was employed as a substrate in the presence of cyclohexene, 3°/2° ratio[14] of adamantane oxygenation was determined to be 4, which was different from that of the reaction using TBHP (10) or MCPBA (26).[15] This value suggests that a ruthenium species is not involved in this process.

In order to gain more mechanistic insights into this catalytic oxygenation by the ruthenium dimer **1**, we examined some effects on the addition of certain trapping reagents described bellow. In the presence of 2,6-di-*t*-butyl-4-methylphenol (BHT) as a radical scavenger, all the reactions were terminated and no color change was observed for the reaction mixture. In the presence of 100eq of dimethyl sulfide (Me_2S), however, only the epoxidation was quenched and significant change was observed for allylic oxygenation; instead of the epoxide, considerable amount of dimethyl sulfoxide (DMSO) was obtained and cyclohexen-1-ol became dominant over cyclohexen-1-one. These results indicate that free radical formation is critical but 2-electron oxidation species is involved at least in the epoxidation process and probably in the oxidation of the alcohol.

To discuss the factor of the formation of oxidizing species under catalytic conditions, $[RuCl(TPA)(DMSO)]^+$ (**2**)[12,16] having the same unit as a half of **1** and potentially labile solvent molecule was employed as a catalyst toward cyclohexene oxygenation. In this case, no reaction was observed for both the catalyst and the substrate. This is probably due to the difference of redox potentials between **1** and **2** in CH_3CN; +0.22 V ($Ru^{II}Ru^{II}/Ru^{II}Ru^{III}$) and +0.71 V ($Ru^{II}Ru^{III}/Ru^{III}Ru^{III}$) for **1** and +0.61 V (Ru^{II}/Ru^{III}) for **2**.[12] The most common mechanism for metal-catalyzed hydrocarbon oxidation is radical-chain autoxidation, in which the the metal ion plays a role to generate free radicals by catalyzing alkyl hydroperoxide decomposition. In our case, the complex **1** having lower redox potential than that of **2** facilitates dioxygen activation toward the formation of alkylhydroperoxide and also reaction (1) as an initiation step of autoxidation of the substrates, compared with non-reactive complex **2**.

$$ROOH + Ru^{II} \rightarrow RO\bullet + OH^- + Ru^{III} \quad (1)$$

This is consistent with our observation that compound **1** activates TBHP toward alkane oxidation but **2** was intact for 1 week in the presence of TBHP.[15] On the other hand, as mentioned above, cyclohexene is oxidized to afford much lower yields for the enol and the enone in the absence of the catalyst; this is due to the absence of dixygen activation step to accelerate the peroxide formation. Therefore, we conclude that cyclohexene is oxidized by molecular oxygen to form cyclohexene-1-hydroperoxide with the aid of complex **1** and the peroxide is decomposed by the ruthenium complex to initiate radical chain mechanism as in eq 1. This kind of autoxidation mechanism has been reported by Gray and coworkers in hydroxylation of alkanes by iron complexes of halogenated porphyrins with molecular oxygen without reductants.[17]

In conclusion, hydrocarbon oxidation was catalyzed by dinuclear ruthenium complex **1** under mild conditions with molecular oxygen and no sacrificial reducing reagents. The main reaction pathway is radical chain mechanism in which the participation of the ruthenium center is suggested in dioxygen activation, peroxide decomposition, and the formation of a two-electron oxidant for the epoxidation and the sulfide oxygenation.

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