Synthesis and Characterization of $[Ru^{III}Cl_2(TPA)]^+$ (TPA = Tris(2-pyridylmethyl)amine) and Its Reactivity toward Alkane Functionalization

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A new ruthenium(III) monomer complex having a tripodal ligand TPA was synthesized and characterized by X-ray crystallography and cyclic voltammetry. The title compound was revealed to catalyze alkane functionalization with *m*-chloroperbenzoic acid.

Ruthenium-catalyzed oxidation of organic compounds has gathered much attention in the light of bioinorganic interests due to their relation to heme and non-heme iron enzymes such as cytochrome P-450 and methane monooxygenase (MMO).[1-4] In the catalytic cycles of those enzymes, high-valent Fe=O intermediates have been postulated[5] and recently some intermediates in the MMO catalysis have been detected.[6,7] Contrary to the Fe=O species, stability of high-valent Ru=O complexes could enable us to examine the direct evaluation of the properties and reactivities of putative and unstable active species and to shed some lights on the iron oxidaton chemistry.

As an attempt to gain mechanistic insights into Ru-catalyzed oxidation reactions which are related to those of Fe compounds, we report herein the synthesis and characterization of a new Ru^{III} mononuclear complex capable of catalyzing alkane functionalization using TPA which has been used for that by Fe^{III} catalysts and revealed to be robust against oxidative degradation.[8]

The title compound $[RuCl_2(TPA)]ClO_4$ (**1**) was synthesized by a modified method of Che and coworkers.[9] Recrystallization of orange powder[10] from water gave orange crystals suitable for X-ray crystallography.[11]

The ORTEP drawing of cation of **1** is shown in Figure 1 with 50% probability thermal ellipsoids. Selected bond lengths and angles are listed in the figure caption. The Ru(III) center possesses a slightly distorted octahedral geometry having ∠N2-Ru-N4 = 163.1(2)°, in which four sites are occupied by TPA and two by chloride anions. The bond distances between Ru and pyridine nitrogens were 2.073(5) and 2.074(5) Å for those two *trans* to each other and 2.087(6) Å for the other. These are slightly shorter than those found in $[Ru(N_4O)(H_2O)](ClO_4)_2$ (**2**) (2.083(5)-2.101(5) Å) (N_4OH = bis(2-(2-pyridylethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine) synthesized by Che and coworkers;[9] slightly longer than those for $[RuCl_2(bpy)_2]Cl$ (2.045(5)-2.063(5) Å) (bpy = 2,2'-bipyridine) reported by Meyer and coworkers.[12] The tertiary amino nitrogen is bound to the Ru center with distance of 2.068(5) Å, which is shorter than that for **2**. The shortening of bond lengths is due to the lack of strong electron donor ligands such as alkoxo group found in **2** which render the metal center electron-rich and cause electronic repulsion against the ligation of other moieties. The comparison of bond distances between **1** and a bis-μ-chloro dimer $[Ru^{II}Cl(TPA)]_2(ClO_4)_2$ (**3**)[13] indicates that the dπ-pπ* metal to ligand back bonding observed in **3** is reduced and that interaction plays an important role in the coordination of π-acceptors such as pyridine to a metal center. Such a tendency has also been pointed out by Meyer in Ru-bpy complexes.[12] As for chloride anion coordination, the electronic charge of metal center is dominant to determine the bond lengths; the Ru-Cl bond lengths are shorter in $[Ru^{III}Cl_2(bpy)_2]Cl$ than in $[Ru^{II}Cl_2(bpy)_2]$ by 0.101Å.[12]

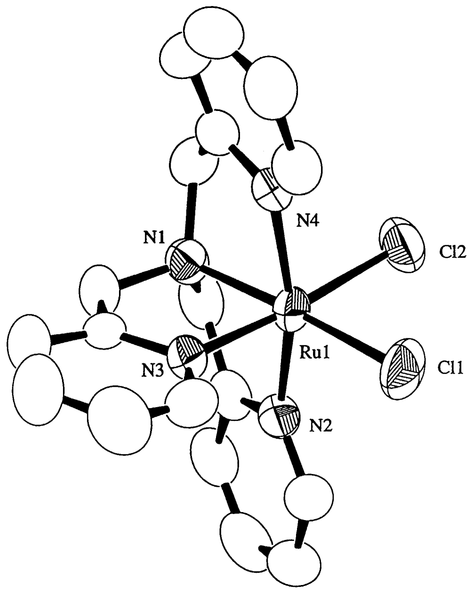

Figure 1. ORTEP drawing of cation of **1** with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Ru-N1, 2.068(5); Ru-N2, 2.074(5); Ru-N3, 2.087(5); Ru-N4, 2.073(5); Ru-Cl1, 2.330(2); Ru-Cl2, 2.357(2); Cl1-Ru-Cl2, 91.21(7); N1-Ru-Cl1, 175.9(2); N1-Ru-N2, 81.3(2); N1-Ru-N3, 82.8(2); N1-Ru-N4, 81.8(2); N2-Ru-N4, 163.1(2); N3-Ru-Cl2, 175.0(2).

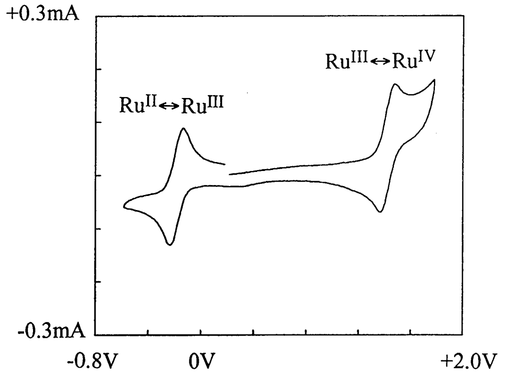

Figure 2. Cyclic voltammogram of $1 \cdot H_2O$ (5.0×10^{-3} M) in CH_3CN in the presence of 0.1 M $n\text{-}Bu_4NClO_4$ at room temperature under N_2; scan rate, 100 mV/s; $Ag/AgNO_3/CH_3CN$ as a reference. The Fc/Fc^+ couple was observed at +51 mV.

The electrochemical property of **1** was investigated by cyclic voltammetry in CH_3CN with 0.1M $n\text{-}Bu_4NClO_4$ as an electrolyte. The complex showed clear two reversible 1-electron redox couples at -0.18 and +1.42V vs $Ag/AgNO_3$, assigned to $Ru^{II} \leftrightarrow$

Table 1. Catalytic turnovers for alkane functionalization by **1** with peroxides[a]

Substrate	Oxidant	Products (turnover numbers)
Cyclohexane	MCPBA	Chlorocyclohexane (3.3) Cyclohexanol (10.3) Cyclohexanone (4.6) Chlorobenzene (9.3)
Adamantane	MCPBA	1-adamantanol (10) 2-adamantanol (0.4) 2-adamantanone (0.9)
Adamantane	TBHP	*No products*

[a] Reactions were performed in CH_3CN under N_2 at room temperature for 24h: [**1**] = 2.0×10^{-3} M, [Cyclohexane] = 1.9 M or [Adamantane] = 0.2 M, [oxidant] = 2.0×10^{-1} M (1M = 1 mol dm^{-3}). Turnover numbers were determined as [product]/[catalyst] by GC analysis with internal standard.

Ru^{III} and $Ru^{III} \leftrightarrow Ru^{IV}$, respectively, as shown in Figure 2. It is intriguing that the complex **1** exhibits the $Ru^{III} \leftrightarrow Ru^{IV}$ couple whereas the dimer **3** shows only $Ru^{II}Ru^{II} \leftrightarrow Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{III} \leftrightarrow Ru^{III}Ru^{III}$ but no redox process to generate $Ru^{III}Ru^{IV}$ species within the CV window.[13] This difference suggests that two σ-donating chlorides bound to one Ru center in **1** lower the potential to generate Ru^{IV} species compared with that of **3** in which two Ru centers share two chlorides. It is also indicated that a reactive intermediate in the **1**-MCPBA system should have a higher oxidation state than +IV to oxidize alkanes.

The catalytic activities of **1** was also examined toward alkane functionalization with peroxides such as *m*-chloroperbenzoic acid (MCPBA) and *t*-butyl hydroperoxide (TBHP) as cooxidants in CH_3CN. The combination of **1** and MCPBA could catalytically oxygenate alkanes such as cyclohexane and adamantane to the corresponding alcohols, ketones, and chlorinated products accompanying the formation of chlorobenzene as shown in Table 1. Similar to the reactions performed by $[FeCl_2(TPA)]ClO_4$ and TBHP,[14] the chlorination of alkanes was observed via an oxidative ligand transfer; however, the stoichiometry of the chlorination in our system is still ambiguous. The 3°/2° ratio[15] in the adamantane oxygenation was 23 which was lower than that of **3**-MCPBA system (34),[13] suggesting the active intermediate in the **1**-MCPBA is less selective than that in **3**-MCPBA system.

On the other hand, **1** showed no oxygenation of adamantane with the use of TBHP. This is in sharp contrast to the fact that **3** can catalyze the oxygenation of alkanes with TBHP probably via electron transfer mechanism to generate free radicals such as *t*-BuO• and *t*-BuOO• as responsible species.[13] Concerning the chlorination by **1** and MCPBA, the mechanism should be similar to that performed by $[FeX_2(TPA)]^+$ (X = Cl, Br, N_3) which is able to transfer one X ligand to alkanes with 1eq of TBHP via the formation of a putative $Fe^V(O)(X)(TPA)$ intermediate.[14]

The identification of reactive intermediate in **1**-MCPBA system is still under way, however, our results suggests that the chlorination and catalytic oxygenation could be conducted by a high-valent Ru=O species in which the Ru center is in +V or +VI oxidation state, which is deduced from CV measurement.

Finally, the compound **1** was revealed to loose Cl^- readily by adding Ag^+ to generate a green complex in H_2O. This procedure will provide an important starting material for a wide range of Ru^{III}(TPA) complexes. On this line, syntheses of a series of complexes are in progress.

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References and Notes

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10 Yield, 85%. Elemental analysis: Found: C, 37.09; H, 3.14; N, 9.45%. Calcd for **1**•H_2O ($C_{18}H_{18}N_4O_4Cl_3Ru$•H_2O): C, 37.28; H, 3.48; N, 9.66%.
11 Crystallographic data for **1**: $C_{18}H_{18}N_4O_4Cl_3Ru$, F_W = 561.79, orthorhombic, $P\,2_12_12_1$, a = 15.527(4) Å, b = 15.823(2) Å, c = 8.782(2) Å, Z = 4, V = 2157.5(7) $Å^3$, D_c = 1.729 g cm^{-3}, μ(Mo Kα) = 11.331 cm^{-1}, R = 0.037, R_W = 0.018, GOF = 1.80. Absolute structure was determined. No water molecule of crystallization was observed in this case.
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15 The 3°/2° ratio = 3×[1-Adamantanol]/{[2-adamantanol]+[2-adamantanone]}