Syntheses and Characterization of Chloro(Me_2SO)ruthenium(II) Complexes with Tris(2-pyridylmethyl)amine or *N*,*N*-Bis(2-pyridylmethyl)glycinate and Their Application for Catalytic Hydroxylation of Alkane

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The new ruthenium(II) complexes, [RuCl(Me_2SO)(TPA)]X (X = Cl or PF_6) and [Ru(BPG)Cl(Me_2SO)] were prepared, and the catalytic activity for alkane hydroxylation using *m*-chloroperbenzoic acid was examined.[2] Two geometrical isomers of the TPA complexes were isolated and showed marked difference in activity: the trans(Cl, N_{amino}) isomer is the most active and selective catalyst toward the oxygenation of adamantane giving 1-adamantanol (75%) and 2-adamantanol (5%).

The development of the highly reactive catalyst capable of oxidizing saturated hydrocarbons under mild conditions is a challenging goal for chemists. Ruthenium complexes have drawn much attention by their high catalytic activity on the oxygenation of alkane.[3] Non-heme iron enzymes such as methane monooxygenase (MMO) are known to catalyze hydroxylation of alkane to alcohol.[4] A number of studies utilizing mononuclear and dinuclear non-heme iron complexes have been reported to realize catalytic alkane functionalization.[5] High valent oxoiron species have been postulated as intermediates of those enzymes and catalysts.[5a,b] Ruthenium is capable of forming compounds in high oxidation state, and oxoruthenium compounds are relatively stable compared to iron compounds and showed catalytic activity on the oxidation of alkane.[6]

We report herein the syntheses and characterization of new ruthenium(II) mononuclear complexes, and their catalytic activity toward alkane hydroxylation in the presence of peracid. The complexes contain chloro and Me_2SO as monodentate ligands and TPA or BPG as a tetradentate ligand: [RuCl(Me_2SO)(TPA)]X (X = Cl (**1**) or PF_6 (**2, 3**)) and [Ru(BPG)Cl(Me_2SO)] (**4**). The iron complexes with TPA or BPG have been examined for catalytic functionalization of alkane.[7] Recently, mononuclear and dinuclear ruthenium complexes, [$RuCl_2$(TPA)]ClO_4 and [RuCl(TPA)]$_2$(ClO_4)$_2$, have also been reported to show catalytic activity,[3g] however, ruthenium complex having two different monodentate ligands has never been examined, to the best of our knowledge.

The chloro(Me_2SO)ruthenium(II) complexes were a mixture of approximately equal amount of two geometrical isomers: trans(Cl, N_{amino}) and cis(Cl, N_{amino}) complexes.[8] Attempts to isolate the isomers of [RuCl(Me_2SO)(TPA)]Cl have failed, however, its hexafluorophosphate salts were successfully separated by fractional recrystallization from acetonitrile-diethyl ether.[9] Complex **2**, which precipitated first, was obtained as yellow crystals suitable for X-ray diffraction study.[10] The ORTEP drawing of the cation of **2** is shown in Figure 1, and selected bond distances and angles are listed in the figure caption. Me_2SO coordinates to the Ru(II) center via S atom *trans* to the tertiary amino nitrogen: complex **2** is cis(Cl, N_{amino}) isomer. Consequently, complex **3** is trans(Cl, N_{amino}) isomer.

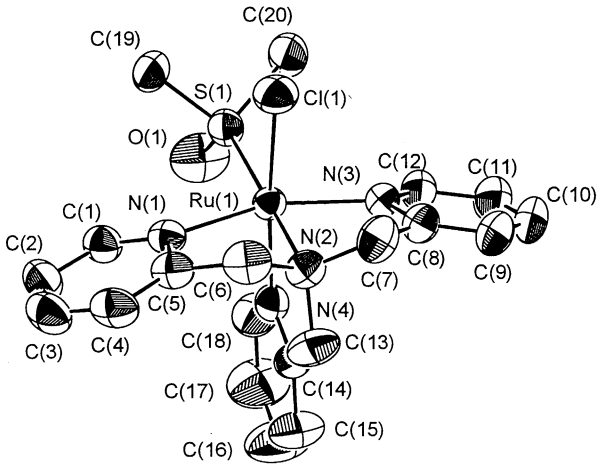

Figure 1. ORTEP drawing of [RuCl(Me_2SO)(TPA)]$^+$ (**2**) with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ru-Cl, 2.433(1); Ru-S, 2.264(1); Ru-N1, 2.079(3); Ru-N2, 2.093(3); Ru-N3, 2.091(3); Ru-N4, 2.062(3); Cl-Ru-S, 85.7(1); N(1)-Ru-N(2), 80.8(1); N(2)-Ru-N(3), 79.9(1); N(2)-Ru-N(4), 81.9(2); N(1)-Ru-N(3), 160.1(1); Cl-Ru-N(4), 172.6(1); S-Ru-N(2), 176.1(1).

The complex has approximate C_s symmetry.

The catalytic oxidation of alkane using the chloro(Me_2SO)ruthenium(II) complexes (**1-4**) with *m*-chloroperbenzoic acid (MCPBA) or *t*-butyl hydroperoxide (TBHP) was examined as listed in Table 1. Adamantane was catalytically oxidized by chloro(Me_2SO)ruthenium complexes with MCPBA to the corresponding alcohol, ketone, and chloroadamantane. No induction period was observed during the reaction. The reactivity depends on the solvent used, and chloroform is the most favorable solvent for this catalytic system: $CHCl_3$ > CH_2Cl_2 > MeCN > Me_2CO. The complex **3** is the most active catalyst: 1-adamantanol (58%) and 2-adamantanol (3%) were obtained (run 9). The C_3/C_2 ratio was 19.[11] Using 50% excess of co-oxidant, yield of 1-adamantanol increased to 75% (run 10).[12] It is noteworthy that two geometrical isomers of [RuCl(Me_2SO)(TPA)]$^+$ complex show marked difference in catalytic activity: the trans(Cl, N_{amino}) isomer **3** is approximately three times more active than the cis(Cl, N_{amino}) isomer **2**. The oxidation reaction using TBHP was less active and selective with **4** or not active with **1**.

The mechanistic studies have not yet been done, however, it should be noted that the two geometrical isomers show different catalytic activity on oxidation of alkane. Consequently, dioxo species can be excluded for the active species of the reaction. We

Table 1. Catalytic oxidation of adamantane by chloro(Me_2SO)ruthenium(II) complexes with MCPBA[a]

Run	Catalyst	Solvent	Yield /%[b]			
			1-ol[c]	2-ol[c]	2-one[c]	1-Cl[c]
1	**1**	Me_2CO	8	trace	1	trace
2	**4**	Me_2CO	7	trace	1	trace
3	**1**	MeCN	6	trace	trace	trace
4	**4**	MeCN	11	2	trace	1
5	**1**	CH_2Cl_2	25	4	2	3
6	**4**	CH_2Cl_2	21	2	2	1
7	**1**	$CHCl_3$	35	3	trace	3
8	**2**	$CHCl_3$	21	3	trace	5
9	**3**	$CHCl_3$	58	3	trace	4
10[d]	**3**	$CHCl_3$	75	5	trace	4
11	**4**	$CHCl_3$	30	3	trace	4
12	--	$CHCl_3$	6	2	trace	3
13[e]	**1**	$CHCl_3$	trace	trace	0	trace
14[e]	**4**	$CHCl_3$	11	5	2	4
15[e]	--	$CHCl_3$	0	0	0	0

[a]The reaction was done at room temperature for 24h: [adamantane] = 4 x 10^{-2} M, [catalyst] = 4 x 10^{-4} M, [MCPBA] = 3 x 10^{-2} M (1 M = 1 mol dm^{-3}). [b]Determined by GC analysis with internal standard based on the substrate. [c]Abbreviations: 1-ol = 1-adamantanol; 2-ol = 2-adamantanol; 2-one = 2-adamantanone; 1-Cl = 1-chloroadamantane. [d][MCPBA] = 6 x 10^{-2} M. [e]TBHP was used instead of MCPBA.

assume that the monooxoruthenium complex may be the active species. Although it is not certain whether chloro or Me_2SO ligand is first replaced by MCPBA, the ligand trans to the oxo group, which should be amino or pyridine group, is likely to have a significant influence on the activity. Further studies are now in progress.

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References and Notes

1 A part of this study has been presented at the 70th Annual Meeting of the Chemical Society of Japan, Tokyo, 1996, Abstr., 1PB050.

2 Abbreviations: TPA = tris(2-pyridylmethyl)amine; BPG = *N,N*-bis(2-pyridylmethyl)glycinate.

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8 Complex **1** were isolated as chloride salt, [RuCl(Me_2SO)(TPA)]Cl · H O: Yield 80%. *Anal.* Found: C, 43.01; H, 4.69; N, 10.03. Calcd for $C_{20}H_{24}Cl_2N_4ORuS$: C, 42.72; H, 4.80; N, 9.76. $(M\text{-}Cl)^+$ 505. Complex **4**, RuCl(Me_2SO)(BPG): Yield 40%. *Anal.* Found: C, 39.36; H, 4.46; N, 8.06. Calcd for $C_{16}H_{20}ClN_3O_3RuS \cdot H_2O$: C, 39.30; H, 4.53; N, 8.59. M^+ 471. $E_{1/2}$ (peak separation): +0.93(0.14), +0.49(0.08) V for **1** and **4**, respectively (vs. SCE in CH_3CN, 0.1M Et_4NClO_4).

9 Complex **2**, cis(Cl,N_{amino})-[RuCl(Me_2SO)(TPA)]PF_6 · 1/2MeCN: *Anal.* Found: C, 37.57; H, 3.86; N, 9.28. Calcd for $C_{21}H_{25.5}ClF_6N_{4.5}OPRuS$: C, 37.62; H, 3.83; N, 9.40. $(M\text{-}PF_6)^+$ 505. ^1H NMR: δ(CD_3CN, 270MHz) 3.43 (6H, s) 4.67 (2H, s) 4.77 (2H, d, J=15 Hz) 5.77 (2H, d, J=15) 6.95 (1H, d, J=7.9) 7.16-7.26 (3H, m) 7.46-7.52 (3H, m) 7.74 (2H, t, J=7.8) 8.70 (2H, d, J=5.6) 9.81 (1H, d, J=5.6).
Complex **3**, trans(Cl,N_{amino})-[RuCl(Me_2SO)(TPA)]PF_6: *Anal.* Found: C, 37.13; H, 3.74; N, 8.65. Calcd for $C_{20}H_{24}ClF_6N_4OPRuS$: C, 37.13; H, 3.74; N, 8.65. $(M\text{-}PF_6)^+$ 505. ^1H NMR: δ(CD_3CN, 270MHz) 2.85 (6H, s) 4.49 (2H, s) 4.67 (2H, d, J=15 Hz) 5.41 (2H, d, J=15) 7.12 (1H, d, J=7.9) 7.27-7.32 (3H, m) 7.43 (2H, d, J=7.9) 7.63 (1H, t, J=7.9) 7.77 (2H, t, J=7.8) 8.76 (2H, d, J=5.3) 9.70 (1H, d, J=5.6). $E_{1/2}$ (peak separation): +0.98(0.07), +0.97(0.06) V, for **2** and **3**, respectively (vs. SCE in CH_3CN, 0.1M Et_4NClO_4).

10 Crystallographic data: $C_{21}H_{25.5}ClF_6N_{4.5}OPSRu$, FW = 670.51, monoclinic, *C*2/c, *a* = 19.000(4) Å, *b* = 17.974(4) Å, *c* = 16.262(5) Å, β = 107.65(2) deg, *V* = 5292(2) $Å^3$, Z = 8, D_c = 1.683g/cm^3, μ(Mo Kα) = 8.82 cm^{-1}, *F*(000) = 2696, *R* = 0.032, R_w = 0.032. Data collection was done on a MAC Science MXC18 diffractometer. 4962 reflections were used.

11 C_3/C_2 = [1-adamantanol]/{[2-adamantanol]+[2-adamantanone]}. The ratio is presumably more than 19, because 2-adamantanol (2%) was also obtained by the oxidation with MCPBA even in the absence of the catalyst (run 12).

12 Probably, the most effective ruthenium catalyst on the hydroxylation of adamantane in the literature is the Ru porphrins, Ru(dioxo)(tetramesitylporphyrinato), with N-oxide, as far as we know: 1-adamantanol(68%), 1,3-adamantanediol(25%), and 2-adamantanone(1%) were obtained.[3f]