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Photoassisted oxygenation of alkane catalyzed by ruthenium complexes using 2,6-dichloropyridine *N*-oxide under visible light irradiation†

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Received (in Cambridge, UK) 5th January 2004, Accepted 6th February 2004
First published as an Advance Article on the web 23rd February 2004

The chloro(Me_2SO)ruthenium(II) complexes with tris(2-pyridylmethyl)amine or its derivative catalyses the selective, stereospecific, and photoregulative alkane oxidation in the presence of 2,6-dichloropyridine *N*-oxide under visible light irradiation.

Photocatalysts have drawn much attention, since they are capable of activating the unreactive C–H bonds to functionalize saturated hydrocarbons.[1] Dissociation of a ligand is often a trigger to initiate the reaction catalyzed by transition metal complexes.[1,2] Photochemical ligand exchange and/or isomerizations of ruthenium complexes have been well known. Photosubstitution reactions of polypyridyl ruthenium(II) complexes are generally assumed to occur by excitation in the MLCT region *via* a dissociative mechanism.[3]

Development of the efficient oxidation catalyst for saturated hydrocarbons is a challenging goal for chemists.[4,5] We have studied oxidation of alkanes catalyzed by non-heme ruthenium complexes.[6] Recently, we have found a new ruthenium-catalyzed oxidation reaction of alkanes utilizing 2,6-dichloropyridine *N*-oxide as co-oxidant and m-CPBA (*m*-chloroperbenzoic acid) or Ce(IV) ion as initiator.[6c] It is assumed that the role of the initiator is to oxidize a Ru(II) ion resulting in labilization of a ligand and the key step of the reaction is a dissociation of a ligand in the ruthenium complex. The further reaction with *N*-oxide may form the oxo species.[6c] Katsuki and co-workers reported that the oxidation of alcohols and epoxidation of alkenes catalyzed by nitrosyl(salen) ruthenium complexes under photoirradiation including photorelease of NO.[7,8] In the present study, the light-driven alkane oxygenation reaction catalyzed by ruthenium complexes using *N*-oxide has been investigated.

Photosubstitution reactions of chloro(Me_2SO)ruthenium(II) complex with tris(2-pyridylmethyl)amine (= TPA), *trans*(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl (**1**), have been investigated in Me_2SO and in MeCN.†[6a,9] Although the UV-vis spectrum of **1** in Me_2SO showed no change by photoirradiation, the Me_2SO peak in the NMR spectrum of **1** in Me_2SO-d_6 collapsed by irradiation (Fig. S-1†). The UV-vis spectra in MeCN have changed by photoirradiation with isosbestic points at 264 and 370 nm and become constant after five-min irradiation, as shown in Fig. 1. The NMR spectra in CD_3CN clearly showed a collapse of the coordinated Me_2SO peak and an appearance of the new peak assigned as a free Me_2SO molecule (Fig. S-2†). A single isomer of the chloro(MeCN) complex with TPA was obtained. Fast-atom bombardment mass spectra of the photoreaction products clearly indicated the formation of [RuCl(TPA)(Me_2SO-d_6)]Cl and [RuCl(CD_3CN)(TPA)]Cl.[10] It was concluded that excitation in the MLCT band resulted in the selective substitution of the S-bound Me_2SO ligand by a solvent molecule. It is noteworthy that no isomerization in regard to the geometry was observed in Me_2SO.

Photosubstitution reactions of *trans*(Cl, N_{amino})-[RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO)]Cl (**2**), §which showed high catalytic ability than **1** on alkane oxidation,[6c] have also been examined and the substituted products were obtained as shown below (Fig. S-3, S-4, S-5†).[11,12] A quantum yield for substitution of the Me_2SO ligand of **2** irradiated at 415 nm (Xe lamp) in MeCN was 0.013 ± 0.001 determined by actinometry. In the presence of 4-picoline (10 equiv.) in 1,2-dichloroethane similar UV-vis spectral changes of **2**

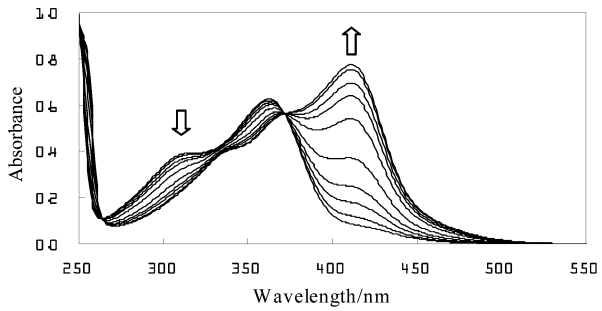
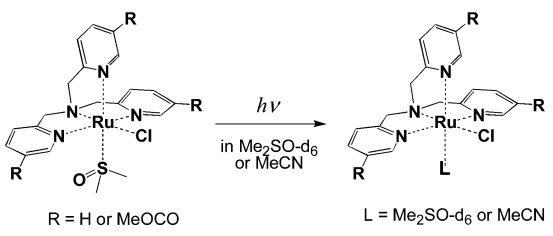


Fig. 1 UV-vis spectral change of chloro((Me_2SO)ruthenium(II) complex, *trans*(Cl, N_{amino})-[RuCl(TPA)(Me_2SO)]Cl (**1**), under photoirradiation in MeCN. 6.7×10^{-5} mol l^{-1}. 0, 3, 8, 15, 30 sec, 1, 1.5, 2, 3, 5 min. λ_{max} (before irradiation): 318 nm(sh); 365 nm. λ_{max} (after irradiation): 336 nm(sh); 368 nm(sh); 411 nm.



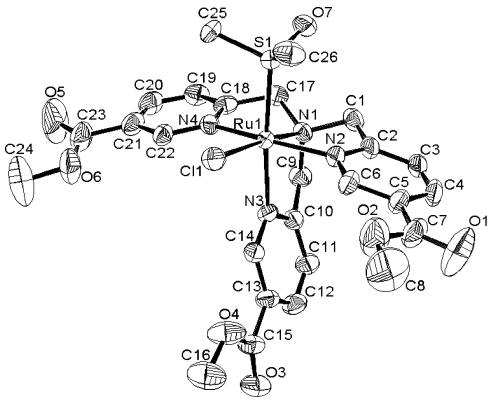


Fig. 2 ORTEP drawing of the cation of *trans*(Cl, N_{amino})-[RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO)]PF_6 (**4**). Thermal ellipsoids are drawn at the 50% probability level.‡

† Electronic supplementary information (ESI) available: syntheses of the complexes, crystallographic data of complex **4** (Table S-1), ^1H NMR spectra before and after irradiation (Fig. S-1, S-2, S-3, S-5), UV-vis spectral change (Fig. S-4, S-6). See http://www.rsc.org/suppdata/cc/b3/b316970g/

DOI: 10.1039/b316970g

with isosbestic points have been observed under photoirradiation (Fig. S-6†). The photoproduct was the corresponding 4-picoline complex.[13]

Since the above experiments clearly demonstrates that the Me_2SO ligand of **1** and **2** selectively dissociates by photoirradiation in the MLCT region, catalytic alkane oxidation catalyzed with ruthenium complex **1** or **2** using 2,6-dichloropyridine *N*-oxide under visible light irradiation (> 385 nm) has been examined.[14] The catalytic oxidation of adamantane using **1** or **2** under irradiation gave 1-adamantanol and adamantane-1,3-diol selectively in good yields (Table 1). No 2-adamantanol was obtained, and only trace amounts of adamantan-2-one and 1-chloroadamantane were detected. The substrate was selectively oxidized at a tertiary carbon. Induction periods were observed: 3 h for **1** and 0.5 h for **2**. No oxidation product was detected without the ruthenium complexes or irradiation. Although efficient alkane oxidation reactions catalyzed by Ru porphyrins with 2,6-dichloropyridine *N*-oxide have been reported,[15] there was no previous report of those catalyzed by non-heme type complexes except ours, as far as we know.[6c,d] Initiators such as *m*-CPBA or Ce(IV) ion were required in the dark reactions, however, no initiator was required in the photoirradiated reactions. It is noteworthy that the reaction under irradiation was significantly faster than that without irradiation in the presence of initiator. Furthermore, hydroxylation of *trans*- or *cis*-decalin at tertiary carbon was also achieved with complete retention of the configuration, giving *trans*- or *cis*-9-decalinol stereospecifically,[16] which suggests that the involvement of the radical species can be excluded as in the case with the Ru porphyrin complexes.[15]

Katsuki *et al*. have reported that irradiation was required only at the initial stage of the reaction in the photooxidation of alcohol catalyzed by a (nitrosyl)ruthenium complex.[7c] If the irradiation is required only for the initiation of the reaction, once the oxidation reaction starts, the reaction proceeds without irradiation. To testify it, the reaction under irradiation with ON/OFF switching was examined. It was found that the reaction was suppressed considerably when the irradiation was turned off, and the oxidation restarted by irradiation. It clearly showed that the reaction is not a photoinitiated one but a photoassisted reaction. This behavior suggests that the irradiation may play a significant role not only in the initiation of the catalytic reaction but also in generating the active species for alkane oxidation. It is for the first time to realize the photoassisted catalytic oxygen transfer from 2,6-dichloropyridine *N*-oxide to alkanes, as far as we know.[17]

In conclusion, we have developed stereospecific and photoregulative catalytic alkane oxidation reactions using chloro(Me_2SO) ruthenium(II) complexes with tris(2-pyridylmethyl)amine or its derivative in the presence of 2,6-dichloropyridine *N*-oxide under visible light irradiation. Further studies on application of this reaction and mechanistic investigations are now in progress.

Table 1 Catalytic oxidation of adamantane catalyzed by complex **1** or **2** with 2,6-dichloropyridine *N*-oxide under visible light irradiation[a]

Catalyst	Time/h	1-Adamantanol (%)[b]	Adamantane-1,3-diol (%)[b]	TON
1	24	46	9	128
2	4	78	13	208
2[c]	24	0	0	0
2[d]	24	65	18	202

[a] Conditions: the reaction was carried out under visible light irradiation (> 385 nm) in 1,2-dichloroethane under nitrogen at room temperature. [adamantane] = 0.04 mol l^{-1}. The ratio of adamantane–2,6-dichloropyridine *N*-oxide–catalyst was 200 : 300 : 1. [b] Determined by GC-MS with internal standard based on the substrate. [c] The reaction without irradiation. [d] The reaction without irradiation in the presence of m-CPBA. Adamantane–2,6-dichloropyridine *N*-oxide–catalyst–*m*-CPBA was 200 : 300 : 1 : 10.

We are grateful to Professor Haruo Inoue and Dr. Shinsuke Takagi for help in measurements of the quantum yield and fruitful discussions.

Notes and references

‡ CCDC 230225. See http://www.rsc.org/suppdata/cc/b3/b316970g/ for crystallographic data in .cif or other electronic format.

§ **2**: FAB-MS: $(M - Cl)^+$ 679, $(M - Cl - Me_2SO)^+$ 601. ^1H NMR: δ($CDCl_3$, 270 MHz) 2.93 (6H, s, Me_2SO), 3.95 (6H, s, CH_3OCO), 3.98 (3H, s, CH_3OCO), 5.38 (2H, s, CH_2(ax)), 5.42 (2H, d, J = 15.5 Hz, CH_2(eq)), 5.81 (2H, d, J = 15.5 Hz, CH_2(eq)), 7.64 (1H, d, J = 8.2 Hz, py-H3(ax)), 7.82 (2H, J = 8.2 Hz, py-H3(eq)), 8.17 (1H, dd, J = 2.0, 8.2 Hz, py-H4(ax)), 8.29 (2H, dd, J = 2.0, 8.2 Hz, py-H4(eq)), 9.33 (2H, d, J = 2.0 Hz, py-H6(eq)), 10.29 (1H, d, J = 2.0 Hz, py-H6(ax)). The X-ray structure of the PF_6 salt, complex **4**, is shown in Fig. 2.

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9 Complex **1** was obtained by fractional recrystallizations from MeOH and AcOEt. The solution of **1** in MeCN or Me_2SO was irradiated by a Pyrex-filtered 500 W ultra-high pressure mercury lamp.

10 FAB MS: $(M - Cl)^+$ 505 for **1**; $(M - Cl)^+$ 511 for [RuCl(TPA)(Me_2SO-d_6)]Cl; $(M - Cl)^+$ 471 for [RuCl(CD_3CN)(TPA)]Cl.

11 FAB MS: $(M - Cl)^+$ 685 for [RuCl{5-$(MeOCO)_3$-TPA}(Me_2SO-d_6)]Cl; $(M - Cl)^+$ 645 for [RuCl(CD_3CN){5-$(MeOCO)_3$-TPA}]Cl.

12 The structure of the chloro(MeCN) complexes is tentative, since the position of the MeCN ligand is inconclusive, thus far.

13 FAB MS: M^+ 694 for [RuCl{5-$(MeOCO)_3$-TPA} (4-Mepy)]$^+$.

14 Visible light (> 385 nm) was irradiated, since 2,6-dichloropyridine *N*-oxide decomposed by UV irradiation.

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16 The oxidation of decalin was done under visible light irradiation using 2,6-dichloropyridine *N*-oxide for 5 h in 1,2-dichloroethane at room temperature. With complex **2**, *trans*-9-decalinol from *trans*-decalin (conv. = 13%) and *cis*-9-decalinol from *cis*-decalin (conv. = 71%) were obtained stereospecifically.

17 Groves *et al*. reported the photostimulation (> 560 nm) of the transformation of [Ru(TPFPP)(CO)] to the active catalyst, however, no result of catalytic alkane reaction was provided[15b].