Syntheses of Ruthenium(II) Complexes with Pentadentate Ligands and Catalytic Oxidation of Alkane Using 2,6-Dichloropyridine *N*-Oxide

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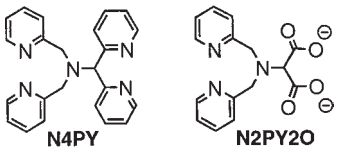
(Received December 20, 2001; CL-011276)

The new ruthenium(II) complexes having pentadentate ligands, [RuCl(N4PY)]Cl and [Ru(N2PY2O) (Me_2SO)] were prepared.[1,2] Catalytic oxidation of adamantane using MCPBA or 2,6-dichloropyridine *N*-oxide as cooxidant has been examined. Using *N*-oxide in the presence of a small amount of MCPBA or Ce(IV) ion (0.5–5 mol% vs substrate) the ruthenium complexes exhibit considerable catalytic activity, and that with the ligand having carboxylate groups is found to be more active.

Development of the highly reactive catalyst having an ability of oxidizing saturated hydrocarbons under mild conditions is a challenging goal for chemists. Non-heme iron enzymes such as methane monooxygenase (MMO) are known as the powerful catalyst for hydroxylation of alkane giving alcohol.[3] A number of studies utilizing non-heme iron or ruthenium complexes have been reported to realize catalytic alkane oxidation.[4] Ruthenium complexes have drawn much attention by their high catalytic activity on the oxidation of alkanes.[5] Previously, ruthenium complexes with tridentate or tetradentate ligands have been frequently employed as the catalysts,[6] however, those with pentadentate ligands have been rarely known.[7]

We report herein the syntheses and characterization of new ruthenium(II) mononuclear complexes with a pentadentate ligand, N4PY or N2PY2O, and their catalytic activity toward alkane oxidation in the presence of MCPBA or 2,6-dichloropyridine *N*-oxide. The new pentadentate ligand N2PY2O having two carboxylate groups was prepared for the first time, as far as we know. The iron complex with N4PY has been examined for catalytic oxidation of alkane,[7] however, ruthenium complexes with a pentadentate ligand has been rarely examined.[8]



The ruthenium(II) complexes were prepared from the reactions of N4PY or N2PY2O and [$RuCl_2(Me_2SO)_4$].[9] The N4PY complex, [RuCl(N4PY)]Cl (**1**), contains chloride as a monodentate ligand, whereas the N2PY2O complex, [Ru(Me_2SO)(N2PY2O)] (**2**), contains Me_2SO. Preliminary X-ray analysis of **2** revealed that Me_2SO coordinated to the Ru(II) center via S atom *trans* to the tertiary amino nitrogen.[10] NMR spectra showed that both complexes had C_s symmetry, confirming that the ligands were both pentadentate.

The catalytic oxidation of adamantane using 0.5 mol% of the ruthenium(II) complexes (**1, 2**) was examined as listed in Table 1. At first, adamantane was catalytically oxygenated by the ruthenium complexes in the presence of MCPBA to the corresponding alcohol in good yields (run 1,2). No induction period was observed during the reaction as shown in Figure 1. The reactivity depends on the solvent used, and chloroform is the most favorable solvent for this catalytic system: $CHCl_3 > CH_2Cl_2 \approx CH_2ClCH_2Cl > MeCN > Me_2CO$. This tendency is similar to that with [RuCl(TPA)(DMSO)]PF_6.[6c] Complex **2**, [Ru(Me_2SO)-(N2PY2O)], is more active than complex **1**, [RuCl(N4PY)]Cl: 1-adamantanol (61%), adamantane-1,3-diol (12%), and 2-adamantanol (1%) were obtained (run 2).

It has been reported that *N*-oxides, mild and highly stable oxidizing reagents, are effective for catalytic alkane oxidation using ruthenium porphyrin complexes.[5c,5e] Next, oxidation reaction using *N*-oxide has also been examined, but adamantane remained intact and no oxidation product was detected (run 8). However, we found that in the presence of a small amount of MCPBA (1–5 mol% vs substrate) catalytic oxygenation has been successfully achieved using *N*-oxide: 1-adamantanol (45–67%) and adamantane-1,3-diol (1–9%) were obtained (run 3–6). Complex **2** is more active than complex **1** as with MCPBA alone. It is assumed that MCPBA acts as an initiator. While 1-chloroadamantane was obtained in the case with MCPBA alone, the reaction with *N*-oxide (+MCPBA) is highly selective to produce almost no 1-chloroadamantane. Although no induction period was observed with MCPBA, induction period (about 2 hours) was observed with *N*-oxide (+MCPBA). Interestingly, when the catalyst was stirred with 5 mol% (vs substrate) of MCPBA for two hours, and then *N*-oxide was added to the reaction mixture, no induction period was observed: 1-adamantanol (68%) and adamantane-1,3-diol (7%) were obtained. It suggests that the reaction of MCPBA and the catalyst produces a Ru(III) intermediate, which is able to react with *N*-oxide giving an oxoruthenium species. In order to prove the above assumption,

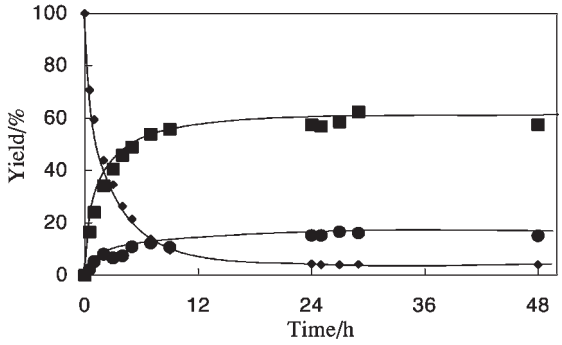


Figure 1. Time profile of oxidation reactions of adamantane catalyzed by complex **2** at room temperature: in the presence of MCPBA alone (subs/cat/MCPBA = 200/1/300). Minor products were omitted for clarity. (◆= adamantane, ■= 1-adamantanol, ●= adamantane-1,3-diol).

Table 1. Catalytic oxidation of adamantane by ruthenium(II) complexes with pentadentate ligands in the presence of MCPBA[a] or 2,6-dichloropyridine *N*-oxide[b]

Run	Catalyst	Cooxidant	Time/h	Temp/°C	Conv/%[c]	Yield/%[c,d]				
						1-ol	2-ol	2-one	1-Cl	1,3-diol
1	[RuCl(N4PY)]Cl	MCPBA[a]	24	rt.	83	40	4	trace	9	6
2	[Ru(N2PY2O)(Me_2SO)]	MCPBA[a]	24	rt.	92	61	1	trace	8	12
3	[RuCl(N4PY)]Cl	*N*-oxide(+MCPBA)[b]	96	50	55	45	0	trace	1	1
4	[RuCl(N4PY)]Cl	*N*-oxide(+MCPBA)[b,e]	120	50	52	60	0	trace	1	4
5	[Ru(N2PY2O)(Me_2SO)]	*N*-oxide(+MCPBA)[b]	120	rt.	83	61	0	0	1	4
6	[Ru(N2PY2O)(Me_2SO)]	*N*-oxide(+MCPBA)[b]	56	50	92	67	0	trace	1	3
7	[Ru(N2PY2O)(Me_2SO)]	*N*-oxide(+Ce(IV))[f]	55	70	76	63	0	trace	1	9
8	[Ru(N2PY2O)(Me_2SO)]	*N*-oxide[g]	24	rt.	0	0	0	0	0	0
9	blank[h]	MCPBA[a]	24	rt.	12	7	1	1	1	0
10	blank[h]	*N*-oxide(+MCPBA)[b]	24	rt.	0	0	0	0	0	0

[a]The reaction was done in $CHCl_3$ under nitrogen: [adamantane] $= 4 \times 10^{-2}$ mol dm^{-3}, [catalyst] $= 2 \times 10^{-4}$ mol dm^{-3}, [MCPBA] $= 6 \times 10^{-2}$ mol dm^{-3} (200/1/300). The concentration of MCPBA was corrected for purity (ca. 70%). [b][adamantane] $= 4 \times 10^{-2}$ mol dm^{-3}, [catalyst] $= 2 \times 10^{-4}$ mol dm^{-3}, [*N*-oxide] $= 6 \times 10^{-2}$ mol dm^{-3}, [MCPBA] $= 2 \times 10^{-3}$ mol dm^{-3} (200/1/300/10). [c]Determined by GC or GC-MS analysis with internal standard based on the substrate. [d]Abbreviations: 1-ol = 1-adamantanol; 2-ol = 2-adamantanol; 2-one = 2-adamantanone; 1-Cl = 1-chloroadamantane; 1,3-diol = adamantane-1,3-diol. [e][MCPBA] $= 4 \times 10^{-4}$ mol dm^{-3} (200/1/300/2). [f]The reaction was done in 1,2-dichloroethane: [adamantane] $= 4 \times 10^{-2}$ mol dm^{-3}, [catalyst] $= 2 \times 10^{-4}$ mol dm^{-3}, [*N*-oxide] $= 6 \times 10^{-2}$ mol dm^{-3}, [Ce(IV)] $= 2 \times 10^{-3}$ mol dm^{-3} (200/1/300/10). See Ref. 11. [g]In the absence of MCPBA or Ce(IV) ion. [h]In the absence of the catalyst.

Ce(IV) ion was added in place of MCPBA (run 7).[11] In the presence of Ce(IV) ion (ten equivalents to the catalyst) the oxidation proceeded as well as that with *N*-oxide and MCPBA. These results suggest that the oxidation to a Ru(III) complex is the key step to initiate the catalytic reaction. *N*-oxide is utilized for the first time in the alkane oxidation catalyzed by non-heme type ruthenium complexes, as far as we know.

Catalytic oxygenation of decalin gave tertiary alcohol, 9-decalinol selectively. The reaction proceeds stereospecifically with complete retention of the configuration as in the case with the Ru porphyrin complex,[5c,5e] that is, *cis*-decalin gave *cis*-9-decalinol, and *trans*-decalin gave *trans*-9-decalinol specifically. These facts suggest that the oxoruthenium complex may be the active species.[12]

Present studies revealed that *N*-oxide is an effective cooxidant for selective alkane oxidation catalyzed by non-heme ruthenium complexes in the presence of the initiator, such as MCPBA or Ce(IV) ion. Further studies are now in progress.

References and Notes

1 A part of this study has been presented at the 2000 International Chemical Congress of Pacific Basin Societies, Honolulu, 2000, Abstr., INOR 650.

2 Abbreviations: N4PY = *N*,*N*-bis(2-pyridylmethyl)-*N*-(bis-2-pyridylmethyl)amine; N2PY2O = *N*,*N*-bis(2-pyridylmethyl)-aminomalonate; TPA = tris(2- pyridylmethyl) amine; MCPBA = *m*-chloroperbenzoic acid; *N*-oxide = 2,6-dichloropyridine *N*-oxide.

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9 Complex **1**, [RuCl(N4PY)]Cl·3H_2O: Yield 70%. Anal. Found: C, 46.82; H, 4.29; N, 11.51%. Calcd for $C_{23}H_{27}Cl_2N_5O_3Ru$: C, 46.55; H, 4.59; N, 11.80. (M-Cl)$^+$ 504. ^{1}H NMR: δ ($CDCl_3$, 270 MHz) 4.42, 4.95 (4H, AB quartet, J = 17.8 Hz, CH_2) 7.05 (2H, d, J = 7.6, 3-*H*-pyCH) 7.15 (2H, dd, J = 4.6, 6.6, 5-*H*-pyCH) 7.21 (2H, dd, J = 5.0, 7.6, 5-*H*-pyCH_2) 7.46 (2H, dd, J = 6.6, 7.6, 4-*H*-pyCH) 7.61 (1H, s, *CH*) 7.76 (2H, dd, J = 7.5, 7.6, 4-*H*-pyCH_2) 8.04 (2H, d, J = 7.5, 3-*H*-pyCH_2) 9.10 (2H, d, J = 5.0, 6-*H*-pyCH_2) 9.45 (2H, d, J = 4.6, 6-*H*-pyCH). Complex **2**, [Ru(N2PY2O)(Me_2SO)]·2H_2O: Yield 22%. Anal. Found: C, 40.01; H, 4.11; N, 8.31%. Calcd for $C_{17}H_{23}N_3O_7RuS$: C, 39.68; H, 4.51; N, 8.17. M$^+$ 479. ^{1}H NMR: δ (D_2O, 270 MHz) 3.44 (6H, s, CH_3SO) 5.08, 5.19 (4H, AB quartet, J = 18.1 Hz, CH_2) 5.19 (1H, s, *CH*COO) 7.21 (2H, dd, J = 5.6, 7.3, 5-*H*-py) 7.37 (2H, d, J = 7.9, 3-*H*-py) 7.67 (2H, dd, J = 7.3, 7.9, 4-*H*-py) 8.91 (2H, d, J = 5.6, 6-*H*-py). $E_{1/2}$ (peak separation): +0.88(0.07), +0.39(0.07) V for **1** and **2**, respectively (vs. Ag/Ag^+ in CH_3CN, 0.1 M Et_4NClO_4).

10 Crystallographic data for complex **2**: $C_{17}H_{19}N_3O_5RuS$, FW = 478.49, orthorhombic, Pbcm, $a = 7.235(5)$ Å, $b = 15.751(5)$ Å, $c = 16.633(5)$ Å, $V = 1895.5(16)$ Å^3, $Z = 4$, $D_c = 1.677$ g/cm^3, μ(Mo Kα) = 9.71 cm^{-1}, $F(000) = 968$, $R = 0.0736$, $R_w = 0.244$. Data collection was done on a Bruker SMART APEX diffractometer. 2262 reflections were used.

11 $(NBu_4)_2Ce(NO_3)_6$ prepared by the literature procedure was employed: H. Zheng, S.-J. Yoon, E. Munck, and L. Que, Jr., *J. Am. Chem. Soc.*, **122**, 3789 (2000).

12 The oxidation reaction of decalin was done for 24 h at room temperature in $CHCl_3$ with MCPBA (Subs/Cat/MCPBA = 200/1/300). Trans/cis ratios of 9-decalinol were determined by GC analysis as follows. With complex **1**, 95/5 for *trans*-decalin (conv = 22%); 11/89 for *cis*-decalin (conv = 57%): with complex **2**, 96/4 for *trans*-decalin (conv = 16%); 6/94 for *cis*-decalin (conv = 58%). In the case with *N*-oxide in the presence of MCPBA (Subs/Cat/*N*-oxide/MCPBA = 200/1/300/10), complete retention of the configuration was observed. With complex **1**, *trans*-9-decalinol from *trans*-decalin (conv = 7%) or *cis*-9-decalinol from *cis*-decalin (conv = 18%) was the sole product.