tert-Butylhydroperoxide epoxidation of alkenes catalysed by ruthenium complex of 1,4,7-trimethyl-1,4,7-triazacyclononane

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Abstract

The complex $[Ru^{III}(Me_3tacn)(OH_2)_2(CF_3CO_2)](CF_3CO_2)_2$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, CF_3CO_2 = trifluoroacetate) is an effective catalyst for the oxidation of organic substrates by tert-butylhydroperoxide. It exhibits high activity and selectivity for alkene epoxidation under mild conditions. A heterolytic O–O cleavage mechanism and an alkylperoxoruthenium(VI) active intermediate are suggested for the catalytic alkene epoxidation.

Keywords: Ruthenium; Oxidation; Alkene epoxidation; Catalyst

1. Introduction

The design of new metal catalysts for selective oxidations of organic molecules is an area of considerable interest in homogenous molecular catalysis [1]. The combined features of economics, selectivity, and safety make tert-butylhydroperoxide (TBHP) as one of the best sources of oxygen atoms for organic oxygenations [2]. Recent advances in the peroxide oxidations include the epoxidation of alkenes and asymmetric epoxidation of allylic alcohols catalysed by CH_3ReO_3 and $Ti(O$-i-$propyl)_4$, respectively [3,4]. In biological systems, fatty acid hydroperoxides are common in living organisms and may participate in biological oxidations [5]. Thus, a study of the metal ion mediated hydroperoxide oxidation reactions may provide insight towards the reactions that occur in biological systems.

Previous studies showed that oxoruthenium complexes are versatile oxidants [6–10]. Groves and Quinn first underlined the use of a sterically bulky ruthenium(II) porphyrin which catalyses aerobic oxidation of alkenes with high stereospecificity at room temperature [10]. However, the low turnovers impede its use to be an effective oxidation catalyst. Thus the search for ruthenium complexes for hydrocarbon oxidations using inexpensive co-oxidants like H_2O_2, TBHP and dioxygen still remain a challenge in the area. Recently, Drago and coworkers demonstrated that the sterically bulky *cis*-$[Ru^{II}(2,9$-$Me_2phen)_2(OH_2)_2]^{2+}$ complex (2,9-Me_2phen = 2,9-dimethyl-phenanthroline) could mediate alkene epoxidation by dioxygen and alkane hydroxylation by hydrogen peroxide [8]. Surprisingly, the use of TBHP in conjunction with ruthenium catalysts for alkene epoxidations has met with limited success by far and the low yields as well as poor selectivities of the organic epoxides so obtained could be reasoned by the

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predominant homolytic autooxidation pathway [11,12]. Herein is described the catalytic activities of $[Ru(Me_3tacn)(OH_2)_2(CF_3CO_2)]$-$(CF_3CO_2)_2$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), which has been shown to be an effective catalyst for selective epoxidation of alkenes by TBHP.

2. Experimental

2.1. Materials

The complex $[Ru(Me_3tacn)Cl_3]$ was synthesized according to the published procedure [13]. tert-Butylhydroperoxide (about 80% in di-tert-butylperoxide) was purchased from Merck and was used as-received. The concentration was determined by iodometric titration. Distilled water was distilled twice from $KMnO_4$. All other solvents and reagents used in syntheses were analytical grade.

2.1.1. $[Ru(Me_3tacn)(OH_2)_2(CF_3CO_2)]$-$(CF_3CO_2)_2$ 1

A mixture of $[Ru(Me_3tacn)Cl_3]$ (0.2 g, 1 eq.) and $Ag(CF_3CO_2)$ (0.45 g, 3.3 eq.) in CF_3CO_2H (25 ml 0.2 M) was refluxed for 1 h. The AgCl thus formed was hot-filtered to give a pale red filtrate. The volume of the filtrate was reduced by slow evaporation. A pale yellow microcrystalline solid was precipitated (ca. 10 ml). Complex 1 was collected on a frit and then dried in vacuo (yield ca. 70%). Elemental analysis: Calc. for $RuC_{15}H_{25}N_3O_8F_9$: C, 27.83; H, 3.89; N, 6.49; Found: C, 27.67; H, 3.58; N, 6.35. UV–vis. [0.2 M CF_3CO_2H, λ_{max}/nm (ϵ_{max}/mol^{-1} dm^3 cm^{-1})]: 286 (1500).

2.1.2. cis-$[Ru(Me_3tacn)O_2(CF_3CO_2)]ClO_4$ 2 · ClO_4

To an ice cooled solution of 1 (0.10 g) in CF_3CO_2H (ca. 10 ml, 0.2 M), a saturated solution of $(NH_4)_2[Ce(NO_3)_6]$ (1 g in 2 ml water) was added. The solution gradually changed to pale green. Addition of a saturated solution of $NaClO_4$ to this pale green solution induced the precipitation of 2 as a pale green microcrys-

talline solid, which was collected on a frit and air dried (yield ca. 55%). Elemental analysis: Calc. for $RuC_{11}H_{21}N_3O_8ClF_3$: C, 25.56; H, 4.10; N, 8.13; Found: C, 25.86, H, 4.01; N, 8.21. UV–vis. [0.2M CF_3CO_2H, λ_{max}/nm (ϵ_{max}/mol^{-1} dm^3 cm^{-1})]: 329 (2400), 675 (50).

Caution: Complex 2 was isolated as a perchlorate salt, which is potentially explosive and should be handled in small amounts.

2.2. Physical measurements and instrumentation

UV–vis. absorption spectra were recorded on a Milton Roy (Spectronic 3000 Array) Diode array spectrophotometer. IR spectra were obtained on a Nicolet model 20 FXT FT–IR spectrophotometer as nujol-mulls ($4000–400$ cm^{-1}). ^{1}H-NMR spectra were run on a JEOL model FX 270 Q spectrometer.

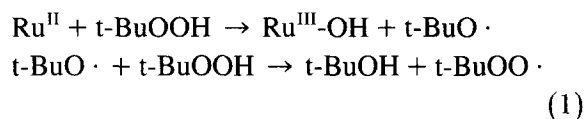### 2.3. General procedure for tert-butylhydroperoxide oxidation of hydrocarbons

In a typical run, a mixture of organic substrate (1 mmol) and TBHP (1 mmol) in dichloromethane (10 cm^3) was stirred at 25°C. Complex 1 or 2 (0.01 mmol) was added to the mixture which was subsequently stirred for 8 to 12 h. A blank containing the same amount of solvent, substrate and TBHP but without the metal catalyst was simultaneously stirred under identical conditions. After addition of internal standard, the aliquot was taken for quantification with GLC or NMR analysis. Gas chromatographic analyses were conducted by using a Hewlett–Packard 5890 series II with flame ionisation detector and a HP-17 column (cross-linked 50% PhMe Silicone, 0.2 μm film thickness). High purity grade nitrogen was used as carrier gas. Component identification was established by comparing the retention time with the authentic samples as well as gas chromatographic mass spectral analysis. Quantification of individual gas chromatographic components was performed by an internal standard method employing a Hewlett–Packard 3396 series II elec-

tronic integrator. The yields of the catalytic oxidations were calculated based on the amount of substrate used.

3. Results and discussion

The synthesis of the complex $[Ru(Me_3tacn)(OH_2)_2(CF_3CO_2)](CF_3CO_2)_2$ (1) was achieved by reacting $[Ru(Me_3tacn)Cl_3]$ with 3 eq. of $Ag(CF_3CO_2)$ in 0.2 M trifluoroacetic acid. It was isolated as a pale yellow solid in a high yield.

Our previous work revealed that the Ru(II) complexes, cis-$[Ru^{II}(6,6'$-$Cl_2bpy)_2(OH_2)_2]^{2+}$ (6,6'-Cl$_2$bpy = 6,6'-dichloro-2, 2'-bipyridine) [11] and $[Ru^{II}(terpy)(6,6'$-$Cl_2bpy)(H_2O)]^{2+}$ (terpy = 2,2':6',2"-terpyridine) [12], are able to catalyse oxidation of alkenes by TBHP. Unfortunately, the organic epoxides were obtained in a relatively low yield and significant loss of stereochemistry with respect to the starting alkene had been observed in some cases. These were attributed to the radical-chain reaction(s) arising from the homolytic cleavage of the O–O bond (Eq. (1))

$$Ru^{II} + \text{t-BuOOH} \rightarrow Ru^{III}\text{-OH} + \text{t-BuO} \cdot$$
$$\text{t-BuO} \cdot + \text{t-BuOOH} \rightarrow \text{t-BuOH} + \text{t-BuOO} \cdot$$

$$(1)$$

Recently, the cis-$[Ru(Me_3tacn)$-$O_2(CF_3CO_2)]ClO_4$ complex has been prepared by Ce^{IV} oxidation of 1. It has been shown to be a versatile oxidant for organic oxidations. Some of its reactions with organic molecules in the presence of TBHP have also been communicated [14]. In this work, we find that alkene epoxidation and ketonization of methylene with TBHP catalysed by 1 exhibit high product yields and selectivities. The results based on the catalyst/oxidant/substrate ratio of 1/100/100 are summarized in Table 1.

Norbornene was oxidized to exo-norbornene oxide exclusively without the formation of $endo$-epoxide, cyclohexene carboxaldehyde or norcamphor. With cyclohexene, epoxidation

prevailed over allylic oxidation and cyclohexene oxide was the major product. For the oxidation of styrene, styrene oxide was the predominant product though a minor formation of benzaldehyde has also been found. The turnover number for styrene oxide could be over 900 using the catalyst/oxidant/substrate ratio of 1/1000/1000 and when this ratio increased to 1/8000/8000, the turnover number increased to well over 6000 after 300 h. The results are summarized in Table 2. Such a high turnover number is remarkable. Recently, Traylor et al. also reported the hemin system to be an effective catalyst for the epoxidation of norbornene by TBHP. However, using this system, a significant loss of stereochemistry was still observed in the epoxidation of cis-β-methylstyrene [15]. In this work, however, epoxidation of cis-β-methylstyrene, cis-stilbene, $trans$-β-methylstyrene and $trans$-stilbene were found to give the corresponding epoxides in high yields and with high stereoselectivity (entries 3–6 in Table 1). In all cases, benzaldehyde, which is one of the C=C bond cleavage products, was detected in a minor amount. The yields of the organic epoxides as well as their stereoselectivity are not affected by the presence of the radical scavenger, 2,6-di-tert-butyl-4-methylphenol. These findings cannot be reconciled with the homolytic cleavage of the O–O bond. This is because reaction of cis-alkene with tert-butylperoxy radical would give the t-BuOOCHR-CHR' · intermediate which undergoes C–C bond rotation before expulsion of t-BuO · [16] (Eq. (2)).

$$(2)$$
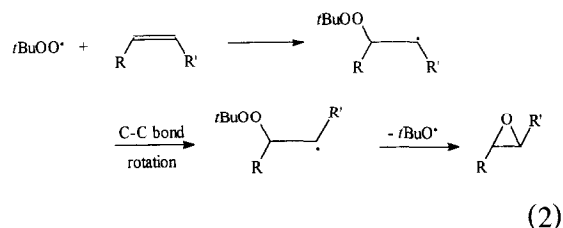
In the reaction with limonene, the 1,2-epoxide arising from the epoxidation at the more elec-

Table 1

Oxidation of various organic substrates (1 mmol) by TBHP (1 mmol) in dichloromethane (10 ml) and in the presence of **1** (0.01 mmol) at 25°C

Entry	Substrate	Product(s)	Yield (%) [a]	Turnover [b]
1	Styrene	Styrene oxide	78	88
		Benzaldehyde	7	
		Phenylacetylaldehyde	3	
2	Styrene [c]	Styrene oxide	79	88
		Benzaldehyde	6	
		Phenylacetylaldehyde	3	
3	trans-Stilbene	trans-Stilbene oxide	54	62
		Benzaldehyde	8	
4	cis-Stilbene	cis-Stilbene oxide	60	68
		trans-Stilbene oxide	3.5	
		Benzaldehyde	4	
5	trans-β-Methylstyrene	trans-β-Methylstyrene oxide	55	67
		Benzaldchyde	12	
6	cis-β-Methylstyrene	cis-β-Methylstyrene oxide	70	77
		trans-β-Methylstyrene oxide	3	
		Benzaldehyde	4	
7	Norbornene	exo-2,3-Epoxynorbornane	72	72
8	Cyclooctene	Cyclooctene oxide	90	90
9	Cyclohexene	Cyclohexene oxide	85	88
		Cyclohexen-2-ol	3	
10	(+)-Limonene	cis-1,2-Limonene oxide	39	71
		trans-1,2-Limonene oxide	15.5	
		8,9-Limonene oxide	16	
11	Cyclohexane [d]	Cyclohexanone	0.25 mmol	73 ($k_H/k_D = 4.5$)
		Cyclohexanol	0.23 mmol	
12	Cyclohexane [e]	Cyclohexanone	0.28 mmol	78
		Cyclohexanol	0.22 mmol	

Reaction time 8 h.

[a] Based on the amount of substrate used.

[b] Based on the ratio of mol of oxidised products formed to mol of metal catalyst used.

[c] 2,6-di-tert-butyl-4-methylphenol (50 mg) was added.

[d] Reaction condition: cyclohexane (2 g), TBHP (1.0 ml) and **1** (0.01 mmol) in CH_2Cl_2 for 16 h.

[e] Reaction condition: cyclohexane (2 g), cumene hydroperoxide (80% v/v, 1.0 ml) and **1** (0.01 mmol) in CH_2Cl_2 for 16 h.

Table 2

Oxidation of styrene by TBHP in dichloromethane and in the presence of **1** at various catalyst/oxidant/substrate ratios. Temperature at 25°C

Entry	Catalyst/oxidant/ substrate	Reaction time/h	Turnovers of epoxide [a]
1	1/100/100	8	78
2	1/1000/1000	24	905
3	1/8000/8000	300	6040

[a] Based on the ratio of mol of styrene oxide formed to mol of metal catalyst used.

| limonene | cis-1,2-epoxide | trans-1,2-epoxide | 8,9-epoxide |

Scheme 1.

tron-rich but more hindered double bond is the preferred product though quite a significant amount of the 8,9-epoxide has also been found (Scheme 1, entry 10 in Table 1).

Previous studies by other workers had shown that the ratio of the 1,2 to 8,9-epoxides could be sensitive to the steric environment. For example, the ratio is 19.6 with the Fe(TPP)Cl-PhIO system (TPP = tetraphenylporphyrinato dianion) and it decreases to 6.9 if the more sterically bulky catalyst, Fe(TMP)Cl, is used (TMP = 5,10,15,20-tetramesitylporphyrinato dianion) [17]. Thus, the observed ratio of 3.4 in the present catalytic system (c.f a ratio of 8.9 found in the limonene oxidation by m-chloroperoxybenzoic acid (mcpba)) indicates that the steric requirement is one of the governing factors for the oxidation to occur. It should be noted that the cis:trans ratio for the 1,2-epoxide
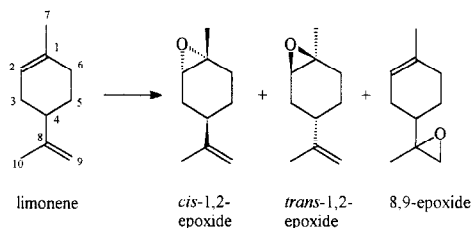
is 2.5:1 which is significantly higher than that of 1:1 for similar reactions with mcpba and that of 1.8 with the Mn(TDCPP)Cl/PhIO system (TDCPP = 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinato dianion) [18]. This would be in good agreement with a more hindered approach of the ruthenium catalyst to the double bond plane on the side cis to the iso-propenyl group.

Study on the competitive oxidations of norbornene and cyclohexene has always been used to probe the nature of the transition state [19]. For those reactions that involve a five-membered intermediate, the norbornene oxide/cyclohexene oxide ratios would lie in the range 72.3 to 8000 whereas for a three-membered reaction intermediate, the ratios are much smaller (1.2–5.5). In this work, a norbornene oxide/cyclohexene oxide ratio of 5 has been found (Table 3), which compares well with that of 5.5 for similar oxidations by CrO_4^{2-} [19].

Table 3

Competitive oxidations of various substrates (5 mmol) by TBHP (1 mmol) in dichloromethane (10 ml) and in the presence of **1** (0.01 mmol)

Entry	Substrates	Products	Yield (mmol)	
1	cis + trans-Stilbene	cis-Stilbene oxide	0.55	cis-/trans-epoxide = 2.2
		trans-Stilbene oxide	0.25	
		Benzaldehyde	0.1	
2	cis + trans-β-Methylstyrene	cis-β-Methylstyrene oxide	0.65	cis-/trans-epoxide = 3.6
		trans-β-Methylstyrene oxide	0.18	
		Benzaldehyde	0.09	
3	Norborene + cyclohexene	Norborene oxide	0.79	Norborene oxide/cyclohexene oxide = 5
		Cyclohexene oxide	0.16	
		Cyclohexen-2-ol	0.01	

Reaction time 8 h.

Table 4

Relative reactivities of oxidation of *para*-substituted styrenes by TBHP in the presence of **1**

p-X-styrene	σ^+	$\log k_{rel}$
OCH$_3$	−0.78	0.608
CH$_3$	−0.31	0.302
H	0	0
Cl	0.11	−0.194
NO$_2$	0.8	−0.790

This implies that the oxygen atom is transferred to the C=C through a three-membered reaction intermediate.

The relative reactivities for the oxidation of *para*-substituted styrenes has also been determined and a linear Hammett plot of $\log k_{rel}$ vs. σ^+ has been found (Table 4). This is shown in Fig. 1. The ρ^+ value is −0.94 which is close to that of −1.04 using mcpba as oxidant and is much smaller than the values of −1.9 to −2.1 that are commonly found for similar oxidations by metal oxo complexes. [20–23]

Cyclohexane can also be oxidized to a mixture of cyclohexanol and cyclohexanone. The results are listed in Table 1. Similar to that found in the PhIO oxidation catalysed by complex **2** [14], the reaction has a rather large primary kinetic isotope effect ($k_H/k_D = 4.5$). This k_H/k_D value is considerably larger than that of 1.1 reported for similar oxidation by ·OH radical [24]. Using cumene hydroperoxide as the terminal oxidant, oxidation of cyclohex-
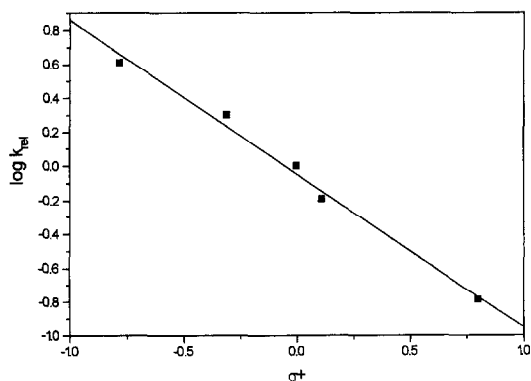
ane yields products similar to the TBHP oxidation (entries 11–12 in Table 1), and acetophenone (formed by the β-scission of 'free' cumyloxyl radical) has not been detected. This suggests that the reactive intermediate is unlikely to be a free organic radical, such as t-BuOO ·, t-BuO · or ·OOH [25].

Fig. 2 shows the time dependence of the formation of styrene oxide, phenylacetaldehyde and benzaldehyde for the TBHP oxidation of styrene in dichloromethane at 25°C. The catalyst/TBHP/styrene ratio used is 1/100/100 and the reaction was completed in 4 h after all TBHP was used up. The first 8 min were found to be an induction period.

The rate of formation of styrene oxide after the induction period is 4.9 μmol min^{-1} which is 26 times faster than that of 0.19 μmol min^{-1} for phenylacetaldehyde. This finding is in accordance with the styrene oxide:phenylacetaldehyde ratio of 26:1 found after the reaction.

Fig. 1. Hammett plot of log k_{rel} versus σ^+ for the epoxidation of *para*-substituted styrenes.
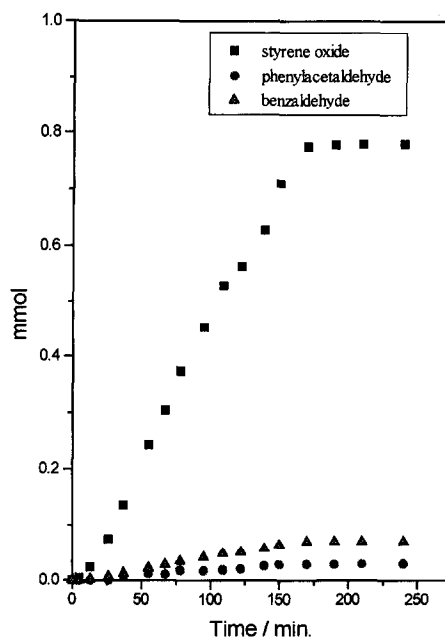

Fig. 2. Time dependence of the formation of styrene oxide, phenylacetaldehyde and benzaldehyde for the TBHP oxidation of styrene dichloromethane. Reaction conditions: catalyst **1** (0.01 mmol), TBHP (1 mmol), styrene (1 mmol); temperature 25°C; dichloromethane (10 ml).

Concerning the reaction mechanism, the involvement of a Ru^{III} active intermediate is quite unlikely, in particular, under the oxidizing conditions employed. In this work, no oxidized product was detected during the induction period. Since tert-butylhydroperoxide is known to be activated by electrophilic metal centre, **1** could be oxidized by TBHP to give an active oxoruthenium species, either $[Ru^{IV}(Me_3tacn)O(OH_2)(CF_3CO_2)]^+$ (here labelled as $Ru^{IV}=O$) or cis-$[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]^+$ (**2**). However, we anticipate that under the oxidizing condition, complex **1** should be oxidized to **2**. Complex **2** could not be the species actually responsible for the oxidations because it was found to oxidize styrene to give benzaldehyde predominately, which is in contrast to the present finding that styrene oxide is the major product in the catalytic oxidation [14]. We propose that the active reaction intermediate is a Ru–OO^{t}Bu species. Reaction of $Ru^{IV}=O$ with TBHP would generate **3** (Eq. 3).


$$(3)$$
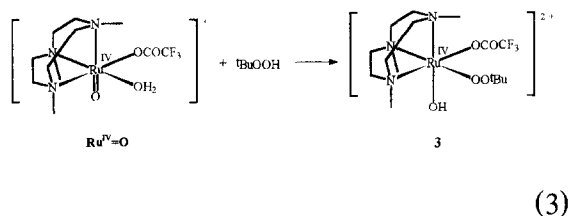
An isoelectronic $Fe^{IV}(OH)(OOH)$ complex had previously been proposed by Sawyer and coworkers to be the reactive intermediate in the iron catalysed oxidation of alkenes and alkanes by hydrogen peroxide [26]. However, complex **3** is likely to play a minor role in the oxidations since it would be easily oxidized to **2**. Our independent studies show that complex **2** also catalyses the oxidation of hydrocarbons by TBHP [14,27]. Thus, we suggest that another reactive intermediate is likely to be formed by the reaction of $[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]^+$ with TBHP. Depending on which oxygen atom coordinates to the Ru centre two activated complexes, **4** and **5**, are possible. The formation of complex **4** is shown in Eq. (4).

$$(4)$$
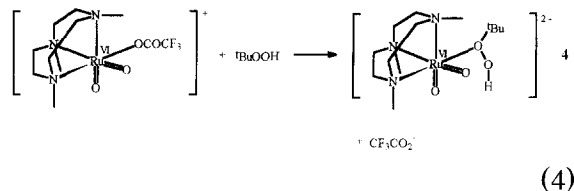
This involves coordination of the metal centre to the more hindered oxygen atom of the hydroperoxide. Unfavourable steric interaction exists between the tert-butyl group and the bulky Me_3tacn ligand. We believe that due to steric reason this activation pathway is not favoured.

The alkylperoxide-ruthenium(VI) complex **5** could be generated by nucleophilic addition of TBHP to the cis-dioxoruthenium(VI) (Eq. 5).

$$(5)$$
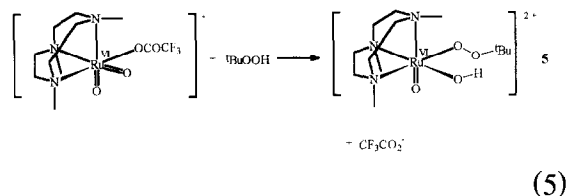
The use of alkylperoxide metal complexes in alkene epoxidations has precedent in literature. For example, alkylperoxide-vanadium(V) complexes of the type $VO(OOBu^t)(ROPhsalR')$ (where $ROPhsalR'$ = tridentate N-(2-oxidophenyl)salicylidenaminato Schiff's base ligand) were reported to epoxidize alkenes to the corresponding epoxides in a stereoselective manner and with high yields [28]. The preferential oxidation of cis-stilbene over that of $trans$-stilbene found in this work could be explained by the unfavourable steric interaction between the phenyl rings and the bulky Me_3tacn ligand, as shown in Fig. 3.
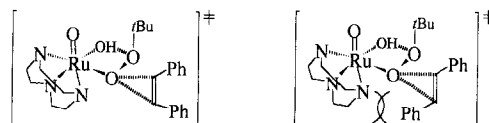

Fig. 3. Transition states of the epoxidation of cis-stilbene and $trans$-stilbene. The N–Me groups are omitted for clarity.

A peroxomolybdenum(VI) complex, MoO-$(O)_2$(HMPA)(H_2O) (HMPA = hexamethyl-phosphoric triamide), has been shown to be a selective oxidant for alkene epoxidation [19,29]. A peroxoruthenium(VI) complex **6**, produced from **5** by elimination of a t-BuOH (Eq. 6) may not be unreasonable, but there has no known example on peroxoruthenium(VI) in literature.
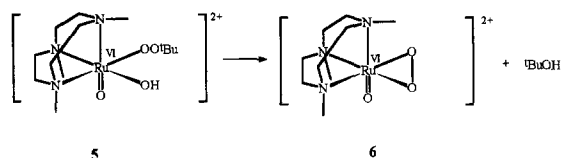
$$\text{(6)}$$

4. Remarks

Complex **1** is able to catalyse alkene and alkane oxidations with TBHP. Its remarkable catalytic activity and selectivity using TBHP as cooxidant have few comparable ruthenium counterparts. We suggest the presence of a labile $CF_3CO_2^-$ in **1** is essential to the TBHP to find a way to coordinate to the ruthenium centre. Another cis-dioxoruthenium(VI) complex, cis-$[Ru^{VI}(tet\text{-}Me_6)O_2]^{2+}$ (tet-Me$_6$ = N,N,N',N'-Tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine) which does not have a labile ligand has been found not to catalyse oxidation of alkenes by TBHP [30].

cis-$[Ru^{VI}(tet\text{-}Me_6)O_2]^{2+}$
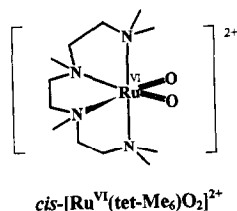
In literature, $RuO_2Cl_3^-$ and $RuO_2Cl_3(OPPh_3)^-$ are more effective catalysts than $[RuO_2Cl_4]^{2-}$ and $[RuO_2Cl_3py]^-$ in the alcohol oxidations [7]. The availability of a vacant coordination site could be invoked to explain the difference in catalysts performance.

Acknowledgements

References

[1] H. Mimoun, In: ed. G. Wilkinson, Comprehensive Coordination Chemistry, Vol. 6 (Pergamon Press, Oxford, 1987) p. 317; R.A. Sheldon and J.K. Kochi, Metal-Catalysed Oxidations of Organic Compounds (Academic Press, New York, 1981).

[2] K.B. Sharpless and T.R. Verhoeven, Aldrichim. Acta 12 (1979) 63; A.S. Rao, In: ed. B.M. Trost, Comprehensive Organic Synthesis, Vol. 7 (Pergamon Press, Oxford, 1991) p. 357.

[3] W.A. Herrmann, R.W. Fischer and D.W. Marz, Angew. Chem. Int. Ed. Engl. 30 (1991) 1638; W.A. Herrmann, R.W. Fischer, M.U. Rauch and W. Scherer, J. Mol. Catal. 86 (1994) 243.

[4] T. Katsuki and K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974; Y. Gao, R.M. Hanson, J.M. Klunder, S.K. Ko, H. Masamune and K.B. Sharpless, J. Am. Chem. Soc. 109 (1987) 5765.

[5] T.J. McMurray and J.T. Groves, In: ed. P.R. Ortiz de Montellano, Cytochrome P-450: Structure, Mechanism and Biochemistry (Plenum Press, New York, 1986) pp. 1–28.

[6] C.M. Che and V.W.W. Yam, Adv. Inorg. Chem. 39 (1992) 233; C.M. Che, Pure and Appl. Chem. 67 (1995) 225.

[7] W.P. Griffith, Chem. Soc. Rev. 21 (1992) 379.

[8] C.L. Bailey and R.S. Drago, J. Chem. Soc. Chem. Commun. (1987) 179; A.S. Goldstein and R.S. Drago, J. Chem. Soc. Chem. Commun. (1991) 21; R.S. Drago, A.S. Goldstein and R.H. Beer, J. Am. Chem. Soc. 116 (1994) 2424.

[9] T.J. Meyer, J. Electrochem. Soc. 131(7) (1984) 221c; M.S. Thompson, F. DeGiovani, B.A. Moyer and T.J. Meyer, J. Org. Chem. 25 (1984) 4972.

[10] J.T. Groves and R. Quinn, J. Am. Chem. Soc. 107 (1985) 5790.

[11] T.C. Lau, C.M. Che, W.O. Lee and C.K. Poon, J. Chem. Soc. Chem. Commun. (1988) 1406.

[12] C.M. Che, C. Ho and T.C. Lau, J. Chem. Soc., Dalton Trans. (1990) 967.

[13] P. Chaudhuri, B.D. Vedora, K. Wieghardt, B. Nuber and J. Weiss, Inorg. Chem. 28 (1989) 459.

[14] W.C. Cheng, W.Y. Yu, K.K. Cheung and C.M. Che, J. Chem. Soc., Chem. Commun. (1994) 1063.

[15] T.G. Traylor, S. Tsuchiya, Y.-S. Byun and C. Kim, J. Am. Chem. Soc. 115 (1993) 2775.

[16] G.X. He and T.C. Bruice, J. Am. Chem. Soc. 113 (1991) 2747.

[17] J.T. Groves and T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 5786.

[18] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, J. Am. Chem. Soc. 110 (1988) 8462.

[19] K.B. Sharpless, J.M. Townsend and D.R. Williams, J. Am. Chem. Soc. 94 (1972) 295.

[20] M.A. Brook, J.R. Lindsay Smith, R. Higgins and D. Lester, J. Chem. Soc., Perkin Trans. 2 (1985) 1049.

[21] J.T. Groves and Y. Wantanabe, J. Am. Chem. Soc. 108 (1986) 507.

[22] C.M. Che, W.T. Tang, W.O. Lee, K.Y. Wong and T.C. Lau, J. Chem. Soc., Dalton Trans. (1992) 1551.

[23] E.G. Samsel, K. Srinivasan and J.K. Kochi, J. Am. Chem. Soc. 107 (1985) 7606; J.M. Garrison, D. Ostovic and T.C. Bruice, J. Am. Chem. Soc. 111 (1989) 4960.

[24] E.S. Rudakov, L.K. Volkova and V.P. Tret'yakov, React. Kinet. Catal. Lett. 16 (1981) 333; G.V. Buxton, C.L. Greenstock, W.P. Helman and A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.

[25] D.W. Snelgrove, P.A. MacFaul, K.U. Ingold and D.W.M. Wayner, Tetrahedron Lett. 37 (1996) 823.

[26] H.C. Tung, C. Kang and D.T. Sawyer, J. Am. Chem. Soc. 114 (1992) 3445.

[27] W.C. Cheng, PhD Thesis, The University of Hong Kong. (1995).

[28] H. Mimoun, M. Mignard, D. Brechot and L. Saussine, J. Am. Chem. Soc. 108 (1986) 8711.

[29] H. Mimoun, I. Seree De Roch and L. Sajus, Tetrahedron 26 (1970) 37.

[30] C.K. Li, C.M. Che, W.F. Tong, T.F. Lai and K.Y. Wong, J. Chem. Soc., Dalton Trans. (1992) 2109.