

A Novel *cis*-Dioxoruthenium(vi) Complex of *N,N',N''*-Trimethyl-1,4,7-triazacyclononane (Me_3tacn) for Organic Oxidation

Wing-Chi Cheng, Wing-Yiu Yu, Kung-Kai Cheung and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

The X-ray structure of $[\text{Ru}(\text{Me}_3\text{tacn})\text{O}_2(\text{CF}_3\text{CO}_2)]^+$ shows a *cis*-dioxoruthenium(vi) unit with the Ru=O distances and O–Ru–O angle being 1.717(9) and 1.715(9) Å and 118.3(4)° respectively, this Ru^{VI} complex catalyses alkene epoxidation and alkane hydroxylation by PhIO and Bu^tOOH.

Recent studies by various groups^{1–3} have established the novel oxidation chemistry of high-valent Ru=O complexes, which are isolable with the Ru ion in different oxidation states and with different auxiliary ligands. An important feature of these complexes is their capability to oxidize C–H and C=C bonds under mild conditions. Although *trans*-dioxoruthenium(vi) complexes of sterically bulky porphyrins are known to catalyse aerobic epoxidation of alkenes,⁴ the quest for a nonporphyrin Ru=O catalyst for alkene epoxidation by inexpensive terminal oxidants such as H₂O₂, Bu^tOOH or O₂ still remains a challenge in this area. Our recent work revealed that the Me₃tacn ligand is well suited for the design of highly oxidizing and sterically bulky Ru=O complexes.⁵ Here we describe a *cis*-dioxoruthenium(vi) complex of Me₃tacn, which can function as a four-electron oxidant and an effective catalyst for epoxidation of alkenes and hydroxylation of alkanes.

The reaction of $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]^6$ with AgCF₃SO₃ in CF₃CO₂H (0.2 mol dm⁻³) gave $[\text{Ru}(\text{Me}_3\text{tacn})(\text{OH}_2)_2(\text{CF}_3\text{CO}_2)](\text{CF}_3\text{SO}_3)_2$, **1**† which was isolated as a pale-yellow solid. Addition of an excess of (NH₄)₂[Ce(NO₃)₆] to a solution of **1** in CF₃CO₂H (0.2 mol dm⁻³) at room temp. gave a green solution, from which $[\text{Ru}(\text{Me}_3\text{tacn})\text{O}_2(\text{CF}_3\text{CO}_2)]\text{ClO}_4$ **2**† was isolated upon addition of NaClO₄. Complex **2** is a diamagnetic light-green crystalline solid, which is stable in the solid state for several hours at room temp. The IR spectrum shows two peaks at 842 and 856 cm⁻¹, assigned to the ν_{asym} and ν_{sym} stretches of the *cis*-dioxoruthenium(vi) unit and its structure has been established by X-ray analysis.‡ Fig. 1 shows a perspective view of the complex cation, featuring one of the few structures of *cis*-dioxoruthenium(vi). The two Ru=O bonds have indistinguishable lengths. The O(2)–Ru–O(3)

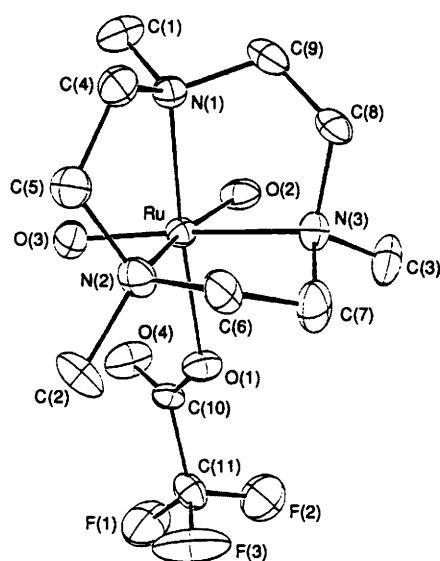


Fig. 1 A perspective drawing of the *cis*- $[\text{Ru}^{\text{VI}}(\text{Me}_3\text{tacn})\text{O}_2(\text{CF}_3\text{CO}_2)]^+$ cation. Selected bond distances (Å) and angles (°): Ru–O(1) 2.046(7), Ru–O(2) 1.717(9), Ru–O(3) 1.715(9), Ru–N(1) 2.097(9), Ru–N(2) 2.23(2), Ru–N(3) 2.197(9); O(1)–Ru–O(2) 93.4(4), O(1)–Ru–O(3) 94.1(4), O(2)–Ru–O(3) 118.3(4), N(1)–Ru–O(2) 90.6(4), N(1)–Ru–N(3) 82.7(4), N(1)–Ru–O(1) 170.3(3).

angle of 118.3(4)° is not unusual for *cis*-dioxoruthenium(vi).^{7,8} The Ru–O(CF₃CO₂) distance of 2.046(7) Å compares well with the related Ru^{VI}–OH distance of 2.036 Å found in Ba $[\text{RuO}_3(\text{OH})_2]$.⁹

Unlike most macrocyclic Ru^{VI}=O complexes¹⁰ which function as two-electron oxidants in organic oxidation, **2** can act as a four-electron oxidant in some reactions. In acetonitrile, it oxidizes dimethyl sulfide and diphenylacetylene to give significant amounts of the four-electron oxidized products, namely, dimethyl sulfone and benzil respectively (entries 6 and 7 in Table 1). The ruthenium product after the reaction is $[\text{Ru}(\text{Me}_3\text{tacn})(\text{MeCN})_2(\text{CF}_3\text{CO}_2)]^+$, which is isolated as the ClO₄⁻ salt. The oxidation becomes catalytic by addition of PhIO (entries 8 and 9 in Table 2). Preliminary studies revealed that **2** reacts with diphenylacetylene to give an immediate deep-blue solution having a broad absorption band at 660 nm. This species gradually changes to the yellow $[\text{Ru}(\text{Me}_3\text{tacn})(\text{MeCN})_2(\text{CF}_3\text{CO}_2)]^+$. Kinetic studies revealed that the decay of the 660 nm band proceeds through a first-order kinetics with a rate constant of $(1.45 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ at 298 K being independent of the concentration of diphenylacetylene. The result is consistent with Scheme 1 where a metallaoxetene **3** is immediately formed.

Complex **2** functions as an effective stoichiometric oxidant for alkene epoxidation. The reactions are completed within minutes. With *cis*- and *trans*-stilbene, very small amounts of isomerized products has been obtained. Competitive experiments showed that *cis*-stilbene reacts at a rate about 3 times faster than its *trans* counterpart (entry 4 in Table 1). With cyclohexene, a significant amount of cyclohexene oxide (entry 5 in Table 1) is obtained. The epoxidation becomes catalytic by the addition of either PhIO or Bu^tOOH. The results are summarized in Table 2. High stereospecificity and good yields of epoxides are obtained in the case with Bu^tOOH as the terminal oxidant. Notably, in the oxidation of styrene, styrene oxide becomes the major product and this is quite different in

Table 1 Stoichiometric oxidation of various organic substrates (0.1 g) by $[\text{Ru}^{\text{VI}}(\text{Me}_3\text{tacn})\text{O}_2(\text{CF}_3\text{CO}_2)]\text{ClO}_4$ (30 mg) in degassed MeCN (5 ml)

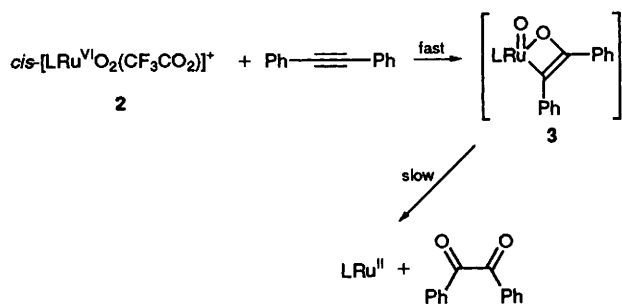
Entry	Substrate	Product(s)	Yield (%) ^a
1	Styrene	Styrene oxide Benzaldehyde	3 76
2	<i>cis</i> -Stilbene	<i>cis</i> -Stilbene oxide <i>trans</i> -Stilbene oxide Benzaldehyde	34 4 37
3	<i>trans</i> -Stilbene	<i>trans</i> -Stilbene oxide Benzaldehyde	5 8
4	<i>cis</i> + <i>trans</i> -Stilbene ^b	<i>cis</i> -Stilbene oxide <i>trans</i> -Stilbene oxide Benzaldehyde	17 7 33
5	Cyclohexene	Cyclohexene oxide Cyclohexen-2-ol Cyclohexen-2-one	32 19 25
6	Dimethyl sulfide	Dimethyl sulfoxide Dimethyl sulfone	91 9
7	Diphenylacetylene	Benzil	60
8	Cyclohexane ^c	Cyclohexanone	56

^a Based on the amount of Ru^{VI}O₂ used. ^b *cis*-Stilbene (0.15 g) + *trans*-Stilbene (0.15 g) (1 : 1) was used as substrate. ^c Solvent: CH₂Cl₂.

Table 2 Catalytic oxidation of various organic substrates (0.2 g) by $[\text{Ru}^{\text{VI}}(\text{Me}_3\text{tacn})\text{O}_2(\text{CF}_3\text{CO}_2)]\text{ClO}_4$ (10 mg) in the presence of either PhIO (0.12 g) or Bu^tOOH (2 ml) as cooxidants in CH_2Cl_2 for 8 h at 25 and 5 °C respectively. The organic products were analysed by ^1H NMR spectroscopy and GC

Entry	Substrate	Product(s)	Turnover ^a (PhIO)	Turnover ^a (TBHP)
1	Styrene	Styrene oxide	5	39
		Benzaldehyde	3.5	16
2	<i>trans</i> -Stilbene	<i>trans</i> -Stilbene oxide	2	20
		Benzaldehyde	1	2
3	<i>cis</i> -Stilbene	<i>cis</i> -Stilbene oxide	5	38
		<i>trans</i> -Stilbene oxide	Trace	3
		Benzaldehyde	3	Trace
4	<i>cis</i> - + <i>trans</i> -Stilbene ^b	<i>cis</i> -Stilbene oxide	4	42
		<i>trans</i> -Stilbene oxide	0.4	25
		Benzaldehyde	3.6	Trace
5	Norbornene	<i>exo</i> -2,3-Epoxyornbornane	7	77
6	Cyclooctene	Cyclooctene oxide	8.5	70
7	Cyclohexene	Cyclohexene oxide	7.5	77
		Cyclohexen-2-ol	2	Nil
		Cyclohexen-2-one	4	13
8	Dimethyl sulfide	Dimethyl sulfoxide	12.5	
		Dimethyl sulfone	6.5	
9	Diphenylacetylene	Benzil	19	
10	Cyclohexane ^c	Cyclohexanone	21	55
		Cyclohexanol	Nil	18

^a Based on the ratio of moles of oxidised products formed: moles of metal catalyst used. ^b *cis*-Stilbene (0.15 g) + *trans*-stilbene (0.15 g) (1:1) was used as substrate. ^c Reaction conditions: cyclohexane (2 g), PhIO (0.4 g)/ Bu^tOOH (2 ml) and $\text{Ru}^{\text{VI}}\text{O}_2$ (12 mg) in CH_2Cl_2 for 16 h.



Scheme 1

the stoichiometric reaction where the major product is benzaldehyde.

In dichloromethane, cyclohexane can also be oxidized by **2** to cyclohexanone (entry 8 in Table 1) although the reaction is comparatively slow. The reaction usually takes more than 12 h for completion. Addition of PhIO or Bu^tOOH makes the oxidation catalytic. Studies on the catalytic oxidation of C_6H_{12} and C_6D_{12} by PhIO catalysed by **2** revealed a primary kinetic isotope effect of 6.5. Such kinetic isotope effect suggests rate limiting C–H bond cleavage and that the reactive intermediate is likely to be $\text{Ru}^{\text{VI}}=\text{O}$ species which reacts with the C–H bond of cyclohexane via a $[\text{Ru}=\text{O}\cdots\text{H}-\text{C}]$ transition state.

Here we have found a macrocyclic $\text{Ru}^{\text{VI}}=\text{O}$ complex which is an effective catalyst for alkene epoxidation and alkane hydroxylation. Because the CF_3CO_2 group in **2** could be labile, it may be possible to have the organic substrate bind to the Ru^{VI} prior to oxidation.

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Footnotes

† Satisfactory elemental analyses were obtained for both **1** and **2**: **1** UV–VIS [$0.2 \text{ mol dm}^{-3} \text{ CF}_3\text{CO}_2\text{H}$, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 286 (1500)]; **2** UV–VIS [$0.2 \text{ mol dm}^{-3} \text{ CF}_3\text{CO}_2\text{H}$, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 329 (2400), 730 (30)].

Crystal data: for **2**, $\text{C}_{11}\text{H}_{21}\text{ClF}_3\text{N}_3\text{O}_8\text{Ru}$, $M_r = 516.82$; monoclinic, space group $P2_1/n$, $a = 8.747(3)$, $b = 13.478(1)$, $c = 15.306(3)$ Å, $\beta = 90.73(2)^\circ$, $V = 1804.2(1.0)$ Å³, $Z = 4$, $D_c = 1.903 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 10.7 \text{ cm}^{-1}$, $F(000) = 1040$. Dimensions: $0.07 \times 0.07 \times 0.45$ mm. The data was collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.7107$ Å) by using the ω - 2θ scan method at 24 °C. Intensity data were corrected for Lorentz and polarization effects and empirical absorption based on the ψ -scan of 4 strong reflections. 2487 Independent reflections were obtained. 1281 Reflections with $F_o > 6.0 \sigma(F_o)$ were considered observed and used in the structural analysis. The structure was solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares using the Enraf-Nonius SPD-1985 Programs on a Micro VAX II computer. Convergence for 244 variables by least squares refinement of F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ was reached at $R = 0.048$ and $wR = 0.056$ and $S = 1.356$ for the 1281 reflections. $(\Delta/\sigma)_{\text{max}} = 0.03$ for atoms of the complex cation. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.01 and 0.65 e Å⁻³ respectively.

Atomic coordinates, thermal parameters, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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