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

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The X-ray structure of $[Ru(Me_3tacn)O_2(CF_3CO_2)]^+$ 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^{t}OOH.

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 H_2O_2, Bu^{t}OOH or O_2 still remains a challenge in this area. Our recent work revealed that the Me_3tacn 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 Me_3tacn, which can function as a four-electron oxidant and an effective catalyst for epoxidation of alkenes and hydroxylation of alkanes.

The reaction of $[Ru(Me_3tacn)Cl_3]$[6] with $AgCF_3SO_3$ in CF_3CO_2H (0.2 mol dm^{-3}) gave $[Ru(Me_3tacn)(OH_2)_2(CF_3CO_2)](CF_3SO_3)_2$, **1**[†] which was isolated as a pale-yellow solid. Addition of an excess of $(NH_4)_2[Ce(NO_3)_6]$ to a solution of **1** in CF_3CO_2H (0.2 mol dm^{-3}) at room temp. gave a green solution, from which $[Ru(Me_3tacn)O_2(CF_3CO_2)]ClO_4$ **2**[†] was isolated upon addition of $NaClO_4$. 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) angle of 118.3(4)° is not unusual for *cis*-dioxoruthenium(VI).[7,8] The Ru–O(CF_3CO_2) distance of 2.046(7) Å compares well with the related Ru^{VI}–OH distance of 2.036 Å found in $Ba[RuO_3(OH)_2]$.[9]

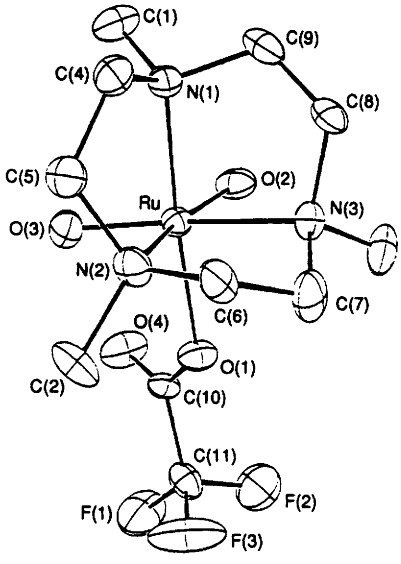


Fig. 1 A perspective drawing of the *cis*-$[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]^+$ cation. Selected bond distances (Å) and angles (°): Ru–O(1) 2.046(7), Ru–O(2) 1.717(9), Ru–O(3) 1.715(9), Ru–N(1) 2.097(9), Ru–N(2) 2.23(2), Ru–N(3) 2.197(9); O(1)–Ru–O(2) 93.4(4), O(1)–Ru–O(3) 94.1(4), O(2)–Ru–O(3) 118.3(4), N(1)–Ru–O(2) 90.6(4), N(1)–Ru–N(3) 82.7(4), N(1)–Ru–O(1) 170.3(3).

Unlike most macrocyclic Ru^{VI}=O complexes[10] 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 $[Ru(Me_3tacn)(MeCN)_2(CF_3CO_2)]^+$, which is isolated as the ClO_4^- 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 $[Ru(Me_3tacn)(MeCN)_2(CF_3CO_2)]^+$. Kinetic studies revealed that the decay of the 660 nm band proceeds through a first-order kinetics with a rate constant of $(1.45 \pm 0.1) \times 10^{-3}$ 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^{t}OOH. The results are summarized in Table 2. High stereospecificity and good yields of epoxides are obtained in the case with Bu^{t}OOH 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 $[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]ClO_4$ (30 mg) in degassed MeCN (5 ml)

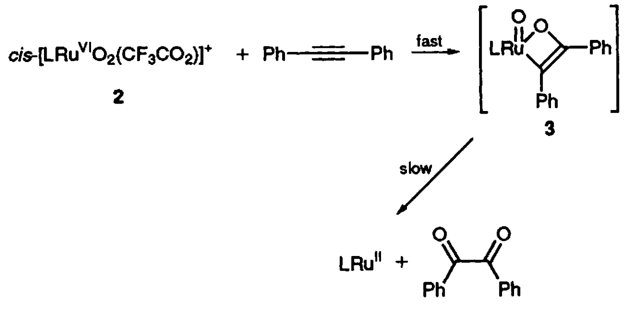
Entry	Substrate	Product(s)	Yield (%)[a]
1	Styrene	Styrene oxide	3
		Benzaldehyde	76
2	*cis*-Stilbene	*cis*-Stilbene oxide	34
		trans-Stilbene oxide	4
		Benzaldehyde	37
3	*trans*-Stilbene	*trans*-Stilbene oxide	5
		Benzaldehyde	8
4	*cis*- + *trans*-Stilbene[b]	*cis*-Stilbene oxide	17
		trans-Stilbene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

[a] Based on the amount of $Ru^{VI}O_2$ used. [b] *cis*-Stilbene (0.15 g) + *trans*-Stilbene (0.15 g) (1 : 1) was used as substrate. [c] Solvent: CH_2Cl_2.

Table 2 Catalytic oxidation of various organic substrates (0.2 g) by $[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]ClO_4$ (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	*trans*-Stilbene	*trans*-Stilbene oxide	2	20
		Benzaldehyde	1	2
3	*cis*-Stilbene	*cis*-Stilbene oxide	5	38
		trans-Stilbene oxide	Trace	3
		Benzaldehyde	3	Trace
4	*cis*- + *trans*-Stilbene[b]	*cis*-Stilbene oxide	4	42
		trans-Stilbene oxide	0.4	25
		Benzaldehyde	3.6	Trace
5	Norbornene	*exo*-2,3-Epoxynorbornane	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 $Ru^{VI}O_2$ (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 cleaveage and that the reactive intermediate is likely to be $Ru^{VI}{=}O$ species which reacts with the C–H bond of cyclohexane *via* a [Ru=O···H–C] transition state.

Here we have found a macrocyclic $Ru^{VI}{=}O$ 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 mol dm^{-3} CF_3CO_2H, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})]: 286 (1500); **2** UV-VIS [0.2 mol dm^{-3} CF_3CO_2H, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})]: 329 (2400), 730 (30).

Crystal data: for **2**, $C_{11}H_{21}ClF_3N_3O_8Ru$, M_r = 516.82; monoclinic, space group $P2_1/n$, a = 8.747(3), b = 13.478(1), c = 15.306(3) Å, β = 90.73(2)°, V = 1804.2(1.0) Å^3, Z = 4, D_c = 1.903 g cm^{-3}, μ(Mo-Kα) = 10.7 cm^{-1}, F(000) = 1040. Dimensions: 0.07 × 0.07 × 0.45 mm. The data was collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 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 $F_o > 6.0\ \sigma\ (F_0)$ 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. $(\Delta/\sigma)_{max}$ = 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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