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Alkene *cis*-Dihydroxylation by [(Me$_3$tacn)(CF$_3$CO$_2$)Ru^{VI}O$_2$]ClO$_4$ (Me$_3$tacn = 1,4,7-Trimethyl-1,4,7-triazacyclononane): Structural Characterization of [3 + 2] Cycloadducts and Kinetic Studies

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Abstract: *cis*-Dioxoruthenium(VI) complex [(Me$_3$tacn)(CF$_3$CO$_2$)Ru^{VI}O$_2$]ClO$_4$ (**1**, Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) reacted with alkenes in aqueous *tert*-butyl alcohol to afford *cis*-1,2-diols in excellent yields under ambient conditions. When the reactions of **1** with alkenes were conducted in acetonitrile, oxidative C=C cleavage reaction prevailed giving carbonyl products in >90% yields without any *cis*-diol formation. The alkene *cis*-dihydroxylation and C=C cleavage reactions proceed via the formation of a [3 + 2] cycloadduct between **1** and alkenes, analogous to the related reactions with alkynes [Che et al. *J. Am. Chem. Soc.* **2000**, *122*, 11380]. With cyclooctene and *trans*-β-methylstyrene as substrates, the Ru(III) cycloadducts [(Me$_3$tacn)(CF$_3$CO$_2$)Ru^{III}O(H)CH(CH$_2$)$_6$HCO]ClO$_4$ (**4a**) and [(Me$_3$tacn)(CF$_3$CO$_2$)Ru^{III}O(H)-PhCHCH(CH$_3$)O]ClO$_4$ (**4b**) were isolated and structurally characterized by X-ray crystal analyses. The kinetics of the reactions of **1** with a series of *p*-substituted styrenes has been studied in acetonitrile by stopped-flow spectrophotometry. The second-order rate constants varied by 14-fold despite an overall span of 1.3 V for the one-electron oxidation potentials of alkenes. Secondary kinetic isotope effect (KIE) was observed for the oxidation of β-d_2-styrene ($k_H/k_D = 0.83 \pm 0.04$) and α-deuteriostyrene ($k_H/k_D = 0.96 \pm 0.03$), which, together with the stereoselectivity of *cis*-alkene oxidation by **1**, is in favor of a concerted mechanism.

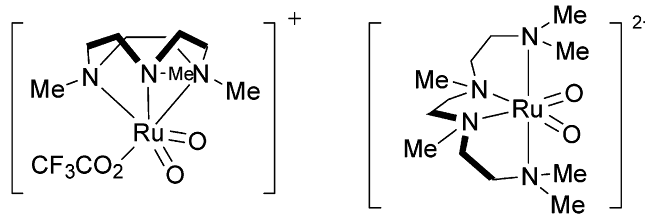
Introduction

Alkene oxidation is a subject of fundamental interest, which profoundly impacts the development of synthetic organic chemistry.[1] For example, *cis*-dihydroxylation of alkenes by OsO$_4$ provides an efficient synthetic route to *cis*-diol products, which are valuable synthetic intermediates for pharmaceuticals.[2] Thus far, practical alkene *cis*-dihydroxylations can only be accomplished using OsO$_4$ as catalyst. Due to the high cost and toxicity of OsO$_4$, there is a need to search for alternative metal catalysts for alkene *cis*-dihydroxylations.[3] A question arises as to whether there could be any alternative metal-oxo catalysts capable of effecting alkene *cis*-dihydroxylation with promises for practical applications. If such a metal-oxo catalyst (other than OsO$_4$) exists, would its reactivity be tuned through variation of auxiliary ligands? In literature[4] only a few structurally characterized *cis*-MO$_n$ ($n \geq 2$) complexes such as OsO$_4$,[2] KMnO$_4$,[5] (L)M^{VII}O$_3$ (L = hydrido-tris-(3,5-dimethylpyrazolyl)-borate, M = Re,[6a] Tc[7a]), Cp*Re^{VII}O$_3$,[6b,c] and [(L)(Cl)Tc^{VII}O$_3$] (L = 1,10-phenanthroline or 2,2′-bipyridine)[7b] are known to react with alkenes by simultaneously transferring two oxygen atoms.

Ruthenium-oxo complexes constitute a family of structurally defined metal-oxo species that are active toward organic

(1) (a) *Modern Oxidation Methods*; Bäckvall, J.-E., Ed.; Wiley-VCH: 2004. (b) Katsuki, T. *Asymmetric Oxidation Reactions: A Practical Approach in Chemistry*; Oxford University Press: 2001. (c) Singh, H. S. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., De Jonge, C. R. H. I., Eds.; Plenum: New York, 1986.
(2) (a) Bolm, C.; Hildebrand, J. P.; Muñiz, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; VCH: New York, 2000; p 399. (b) Kolb, H. C.; Van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (c) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. (d) Gao, Y. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Editor-in-Chief; Wiley: New York, 1995; Vol. 6, p 3801.
(3) For Fe-catalyzed dihydroxylations: (a) Fujita, M.; Costas, M.; Que, L., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 9912. (b) Chen, K.; Costas, M.; Kim, J.; Tipton, A. K.; Que, L., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 3026. (c) Chen, K.; Que, L., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 2227. For Mn-catalyzed dihydroxylations: (d) Brinksma, J.; Schmieder, L.; Van Vliet, G.; Boaron, R.; Hage, R.; De Vos, D. E.; Alsters, P. L.; Feringa, B. L. *Tetrahedron Lett.* **2002**, *43*, 2619. (e) De Vos, D. E.; De Wildeman, S.; Sels, B. F.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 980. For Ru-catalyzed dihydroxylations: (f) Ho, C.-M.; Yu, W.-Y.; Che, C.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3303. (g) Plietker, B.; Niggemann, M. *Org. Lett.* **2003**, *5*, 3353. (h) Shing, T. K. M.; Tam, E. K. W. *Tetrahedron Lett.* **1999**, *40*, 2179. (i) Shing, T. K. M.; Tam, E. K. W.; Tai, V. W. F.; Chung, I. H. F.; Jiang, Q. *Chem.—Eur. J.* **1996**, *2*, 50. (j) Shing, T. K. M.; Tai, V. W. F.; Tam, E. K. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2312.
(4) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(5) (a) Fatiadi, A. J. *Synthesis* **1987**, 85. (b) Lee, D. G. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Editor-in Chief; Wiley: New York, 1995; Vol. 6, p 4274.
(6) (a) Gable, K. P.; Zhuravlev, F. A. *J. Am. Chem. Soc.* **2002**, *124*, 3970. (b) Gable, K. P.; Juliette, J. J. J. *J. Am.* Chem. Soc. **1995**, *117*, 955. (c) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833.

oxidations.[8−11] Being isoelectronic with OsO_4, RuO_4 is a powerful oxidant that cleaves the C=C bond upon reaction with alkenes.[12] Protocols for oxidative C=C cleavage using $RuCl_3$ as a catalyst are well documented in the literature.[3f,13] In 1994, Shing and co-workers reported the $RuCl_3$-catalyzed alkene *cis*-dihydroxylation using $NaIO_4$ as terminal oxidant.[3h−j] Recently, we developed a catalytic protocol for alkene *cis*-dihydroxylation using ruthenium nanoparticles as catalyst.[3f] Among these reported examples, reactive *cis*-dioxoruthenium species have been postulated as the key intermediate responsible for the *cis*-diol formation/C=C bond cleavage. However, the reactions of *cis*-dioxoruthenium complexes with alkenes to give *cis*-1,2-diols remain poorly characterized. Indeed, apart from d^0- and d^1-tetraoxo/trioxo complexes, limited examples on structurally defined *cis*-MO_2 complexes that react with alkenes to give [3 + 2] cycloadducts are known in the literature. Previously we prepared and structurally characterized two *cis*-dioxoruthenium(VI) complexes (Figure 1), $[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**; Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[11a,c] and *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2](ClO_4)_2$ (**2**; Tet-Me_6 = *N*,*N*,*N′*,*N′*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine)[11d] with $E°$ values of 1.1 V ($Ru^{VI/V}$) and 0.8 V ($Ru^{VI/IV}$) vs SCE, respectively. Here we report that complex **1** oxidized alkenes to afford *cis*-1,2-diols (in aqueous medium) and dialdehydes (in nonaqueous medium) in good to excellent yields under stoichiometric conditions. Analogous to the alkyne oxidation,[11a] the [3 + 2] cycloadducts for the reactions of cyclooctene and *trans*-β-methylstyrene with **1** have been isolated and structurally characterized by X-ray crystal analyses. In this work, the cycloaddition reaction has been examined by kinetic studies and organic product analysis.



$[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]^+$ *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2]^{2+}$

Figure 1. *cis*-Dioxoruthenium(VI) complexes.

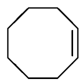
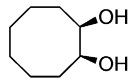
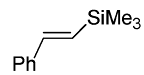
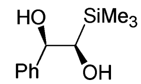
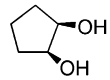
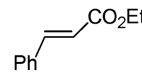
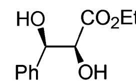
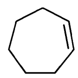
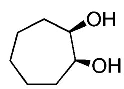
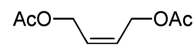
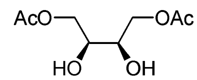
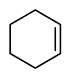
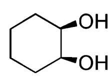
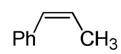
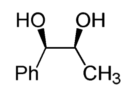
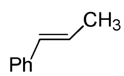
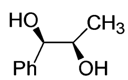
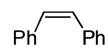
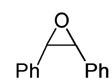
Results

Stoichiometric Alkene *cis*-Dihydroxylations by $[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (1). Treatment of cyclooctene (30 mmol) with **1** (300 μmol) in a *tert*-butyl alcohol−water mixture (10:2 v/v) under an argon atmosphere at room temperature produced *cis*-1,2-cyclooctanediol in 85% isolated yield (Table 1, entry 1); 1,8-octanedialdehyde (C=C bond cleavage product) was obtained in 5% yield. Neither *trans*-1,2-cyclooctanediol nor cyclooctene oxide was detected by NMR analysis of the crude reaction mixture. The yields of the *cis*-1,2-diol and dialdehyde were calculated based on the stoichiometry of Ru/cyclooctene = 1:1. The *cis*-/*trans*-diols and 1,8-octanedialdehyde were identified by their ^1H and ^{13}C NMR signals with reference to the literature data [*cis*-diol: δ_H 3.9 ppm (d, 2H, J = 10 Hz), δ_C = 73.1 ppm. *trans*-diol: δ_H 3.6 ppm (d, 2H, J = 9.5 Hz), δ_C = 76.1 ppm. 1,8-octanedialdehyde: δ_H 9.8 ppm (t, 2H, J = 1.5 Hz), δ_C = 202.5 ppm].[14] After the reaction, $[(Me_3tacn)_2Ru^{III}_2(\mu\text{-}O)(\mu\text{-}CF_3CO_2)_2](ClO_4)_2$ (**3**) was isolated in quantitative yield; this complex has been characterized by X-ray crystal analysis (Figure S1, Tables S1 and S2) [for more detailed characterization of **3**, including its UV−vis spectrum (Figure S2) and structure features, see Experimental Section and Supporting Information]. The observed *cis*-dihydroxylation should be unique for the *cis*-dioxoruthenium(VI) complex, since the analogous cyclooctene oxidation by *trans*-$[Ru^{VI}(N_2O_2)O_2]ClO_4$ (N_2O_2 = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane)[10g] having comparable $E°(Ru^{VI/IV})$ of 0.92 V (vs SCE, pH 1.0) afforded cyclooctene oxide in 90% yield without any *cis*-1,2-diol being detected.

The employment of aqueous *tert*-butyl alcohol as solvent is critical for the *cis*-diol formation. When the reaction of **1** with cyclooctene was undertaken in dry acetonitrile, 1,8-octanedialdehyde was obtained in 91% yield (Table 2, entry 1); neither *cis*-1,2-cyclooctanediol nor cyclooctene oxide was detected by ^1H NMR analysis. However, when aqueous acetonitrile (MeCN/H_2O = 10:1 v/v) was used as solvent, significant *cis*-cyclooctane-1,2-diol formation (in 22% yield) was observed albeit with 1,8-octanedialdehyde being the major product (yield: 60%). In this case, epoxide and *trans*-1,2-diol were not detected according to NMR analysis of the crude reaction mixture. For oxidation of other cycloalkenes, cleavage of the C=C bond to dialdehydes prevailed in dry acetonitrile; details are given in later sections.

(7) (a) Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 231. (b) Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981.
(8) For reviews, see: (a) Che, C.-M.; Lau, T.-C. In *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2004; Vol. 5, Chapter 5.6, p 733. (b) Che, C.-M.; Yu, W.-Y. *Pure Appl. Chem.* **1999**, *71*, 281. (c) Murahashi, S.-I.; Naota, T. In *Comprehensive Organometallic Chemistry II*, Vol. 12; Abel, E. W., Stone, F. G. A., Wilkinson, G. W., Eds.; Pergamon: Oxford, 1995; p 1177. (d) Che, C.-M.; Yam, V. W.-W. *Adv. Inorg. Chem.* **1992**, *39*, 233. (e) Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179. (f) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984.
(9) See, for example, Ru(IV): (a) Lebeau, E. L.; Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10535. (b) Stultz, L. K.; Huynh, M. H. V.; Binstead, R. A.; Curry, M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 5984. (c) Fung, W.-H.; Yu, W.-Y.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7715. (d) Cheng, W.-C.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 57. (e) Ho, C.; Che, C.-M.; Lau, T.-C. *J. Chem. Soc., Dalton Trans.* **1990**, 967. (f) Dobson, J. C.; Seok, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513. Ru(V): (g) Fackler, N. L. P.; Zhang, S.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1996**, *118*, 481. (h) Che, C.-M.; Yam, V. W.-W.; Mak, T. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2284. (i) Dengel, A. C.; Griffith, W. P.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1720.
(10) See for example: (a) Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Masciocchi, N.; Sironi, A.; Cenini, S. *Inorg. Chem.* **2005**, *44*, 2039. (b) Zhang, R.; Yu, W.-Y.; Sun, H.-Z.; Liu, W.-S.; Che, C.-M. *Chem.−Eur. J.* **2002**, *8*, 2495. (c) Liu, C.-J.; Yu, W.-Y.; Che, C.-M.; Yeung, C.-H. *J. Org. Chem.* **1999**, *64*, 7365. (d) Lebeau, E. L.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2174. (e) Lai, T.-S.; Zhang, R.; Cheung, K.-K.; Kwong, H.-L.; Che, C.-M. *Chem. Commun.* **1998**, 1583. (f) Dovletoglou, A.; Meyer, T. J. *J. Am. Chem.* Soc. **1994**, *116*, 215. (g) Che, C.-M.; Tang, W.-T.; Wong, W.-T.; Lai, T.-F. *J. Am. Chem. Soc*. **1989**, *111*, 9048. (h) Perrier, S.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 4165. (i) Che, C.-M.; Wong, K.-Y.; Poon, C.-K. *Inorg. Chem.* **1985**, *24*, 1797. (j) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.
(11) See for example: (a) Che, C.-M.; Yu, W.-Y.; Chan, P.-M.; Cheng, W.-C.; Peng, S.-M.; Lau, K.-C.; Li, W.-K. *J. Am. Chem. Soc.* **2000**, *122*, 11380. (b) Cheng, W.-C.; Yu, W.-Y.; Li, C.-K.; Che, C.-M. *J. Org. Chem.* **1995**, *60*, 6840. (c) Cheng, W.-C.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 1063. (d) Li, C.-K.; Che, C.-M.; Tong, W.-F.; Tang, W.-T.; Wong, K.-Y.; Lai, T.-F. *J. Chem. Soc., Dalton Trans.* **1992**, 2109. (e) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179.
(12) (a) Lee, D. G.; Chen, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S. V., Eds.; Pergamon: Oxford, 1991; Vol. 7, Chapter 3.8, p 541. (b) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1420.
(13) (a) Yang, D.; Zhang, C. *J. Org. Chem.* **2001**, *66*, 4814. (b) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936. (c) Sondheimer, F.; Mechoulam, R.; Sprecher, M. *Tetrahedron* **1964**, *20*, 2473. (d) Stork, G.; Meisels, A.; Davies, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 3419.
(14) Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **1999**, *1*, 713.

Table 1. Stoichiometric Alkene *cis*-Dihydroxylations by **1**[f]

entry	alkenes	products	yield (%)[a]	entry	alkenes	products	yield (%)[a]
1[b]			85	6[e]			70
2			80	7[e]			72
3[c]			66	8			75
4[d]			60	9[e]			84
5[e]			72	10			58
						PhCHO	35

[a] Isolated yield. [b] Yield of 1,8-octanedialdehyde: 5%. [c] Yield of 1,7-heptanedialdehyde: 15%. [d] Yield of 1,6-hexanedialdehyde: 10%. [e] Benzaldehyde (10−15% yield) was detected by capillary GC using the internal standard method. [f] Reaction conditions: To a degassed *tert*-butyl alcohol (10 mL)/water (2 mL) mixture containing alkene (30 mmol) was added **1** (300 μmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 14 h.

The results for the other cycloalkenes are summarized in Table 1. By employing the following reaction conditions, cyclopentene was oxidized to *cis*-1,2-cyclopentanediol in 80% isolated yield (entry 2): **1** (300 μmol), alkene (30 mmol), 80% aqueous *tert*-butyl alcohol under an argon atmosphere. No other oxidized products were detected according to ^{1}H NMR analysis. Oxidation of cycloheptene by **1** furnished the corresponding *cis*-1,2-diol and 1,7-heptanedialdehyde in 66% and 15% yields, respectively (entry 3). According to the previous works,[9−11] cationic oxo-ruthenium complexes containing chelating nitrogen donor ligands would react with cyclohexene via allylic C−H bond oxidation to afford 2-cyclohexen-1-ol and 2-cyclohexen-1-one as major products. In aqueous *tert*-butyl alcohol **1** was found to react with cyclohexene via *cis*-dihydroxylation preferentially, and the corresponding *cis*-1,2-diol was produced in 60% yield (entry 4). Minor products including 1,6-hexanedialdehyde (10%), 2-cyclohexen-1-ol (5%), and 2-cyclohexen-1-one (5%) were detected based on capillary GC analysis.

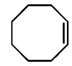
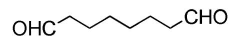
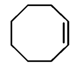
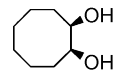
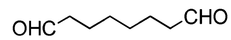
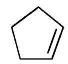
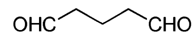
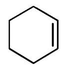
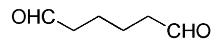
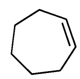
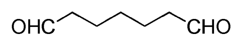
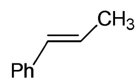
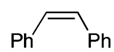
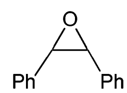
cis-Dihydroxylation of aromatic alkenes has also been achieved using **1** as oxidant. Treating *trans*-β-methylstyrene with **1** in aqueous *tert*-butyl alcohol produced *threo*-1-phenyl-1,2-propanediol in 72% yield with minor benzaldehyde (15% yield) formation (Table 1, entry 5). Again, neither epoxide nor the anti-dihydroxylation product was formed according to NMR analysis of the crude reaction mixture. When *trans*-β-(trimethylsilyl)styrene was subjected to the following conditions, the corresponding syn-dihydroxylation product was formed in 70% yield without formation of epoxides/anti-dihydroxylation product (entry 6): **1** (300 μmol), alkene (30 mmol) in aqueous *tert*-butyl alcohol. This result is comparable to the case when OsO_4 was used as oxidant.[15] Given that electron deficient α,β-unsaturated alkenes such as ethyl cinnamate are poor substrates for oxo-ruthenium oxidants,[8−11] it is striking that **1** can oxidize ethyl cinnamate to afford (±)-*threo*-ethyl 2,3-dihydroxy-3-phenylpropanoate in 72% yield (entry 7).

Dihydroxylation of *cis*-2-butene-1,4-diacetate by **1** proceeded stereoselectively, affording 1,4-di-*O*-acetylerythritol in 75% isolated yield (entry 8). Formation of the anti-isomerized product (i.e., 1,4-di-*O*-acetylthreitol) was not observed based on NMR analysis of the crude reaction mixture. Under similar conditions, the reaction of *cis*-β-methylstyrene with **1** gave *erythro*-1-phenyl-1,2-propanediol in 84% yield (entry 9). Oxidation of *cis*-stilbene by **1** in aqueous *tert*-butyl alcohol afforded *cis*-stilbene oxide in 58% yield and benzaldehyde in 35% yield (entry 10). Neither syn-dihydroxylation product nor *trans*-epoxide was detected by ^{1}H NMR analysis of the crude reaction mixture.

Our earlier works showed that *cis*-[(Tet-Me$_6$)Ru^{VI}O$_2$](ClO$_4$)$_2$ (**2**) with $E°(\mathrm{Ru}^{VI/IV}) = 0.80$ V vs SCE (pH 1.0) can oxidize alkenes and alkanes in acetonitrile under room conditions.[11b] In this work, we found that **2** (300 μmol) reacted with cyclooctene (30 mmol) in aqueous *tert*-butyl alcohol to produce 1,8-octanedialdehyde in 60% yield and *cis*-1,2-cyclooctanediol in 22% yield. Neither *trans*-diol nor epoxide was detected at the end of the reaction. In contrast to the results with **1** being the oxidant, **2** reacted with cyclohexene under identical conditions to give *trans*-1,2-cyclohexanediol in 65% yield and 2-cyclohexen-1-ol in 21% yield. No *cis*-1,2-diol was detected by ^{1}H NMR analysis. Compared to **2**, **1** afforded the *cis*-diol

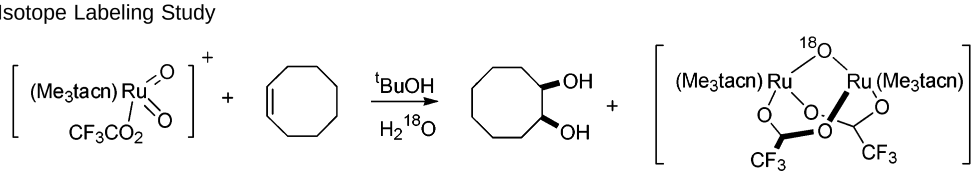
(15) Bassindale, A. R.; Taylor, P. G.; Xu, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1061.

Table 2. Stoichiometric Oxidative C=C Bond Cleavage by **1**[e]

entry	solvent	alkenes	product(s)	yield (%)[a]
1	MeCN			91
2	MeCN + H_2O			22
				60
3	MeCN			73[b]
4	MeCN			70[c]
5	MeCN			80
6	MeCN		PhCHO[d]	85
7	MeCN			45
			PhCHO[d]	32

[a] Isolated yield based on the amount of oxidant used. [b] Yield of *cis*-1,2- cyclopentanediol = 10%. [c] Yield of *cis*-1,2-cyclohexanediol = 14%. [d] Determined by GC. [e] Reaction conditions: To a degassed acetonitrile (10 mL) containing alkene (30 mmol) was added **1** (300 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 14 h.

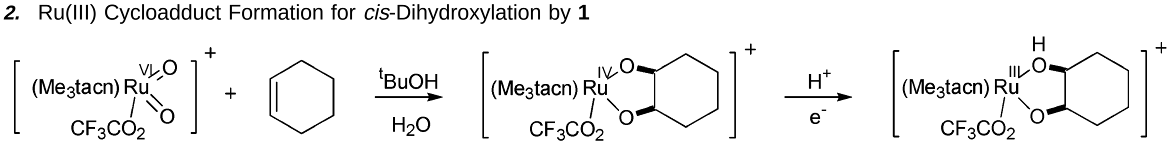
Scheme 1. ^{18}O Isotope Labeling Study



(**3**)

FAB-MS: *m/z* = 889 ([*M* + ClO_4]$^+$)

Scheme 2. Ru(III) Cycloadduct Formation for *cis*-Dihydroxylation by **1**



(**5d**) (**4d**)

products in better yields, and hence subsequent mechanistic studies were performed with **1** as the oxidant. The results for oxidation of other alkenes by **2** are provided in Table S3.

^{18}O Isotope Labeling Experiment. Treatment of cyclooctene (30 mmol) with **1** in a mixture of *tert*-butyl alcohol (10 mL) and $H_2{}^{18}O$ (2 mL) under an inert atmosphere at ambient temperature for 14 h produced *cis*-1,2-cyclooctanediol and 1,8-octanedialdehyde in 85% and 5% isolated yields, respectively; neither the diol nor the aldehyde contained ^{18}O isotope (as shown by MS analysis). On the other hand, FAB-MS (Figure S3) of **3**, isolated in 96% yield by diethyl ether-induced precipitation, revealed the exclusive incorporation of the ^{18}O label in this complex (Scheme 1). We reason that both *cis*-dihydroxylation and oxidative C=C cleavage reactions involved direct interaction between the C=C bond and the two oxo groups of **1**.

Structural Characterization of [3 + 2] Cycloadducts between [(Me$_3$tacn)(CF$_3$CO$_2$)Ru^{VI}O$_2$]ClO$_4$ and Alkenes. In aqueous *tert*-butyl alcohol, cyclohexene (10 equiv) reacted instantaneously with **1** to give a metastable Ru(III) cycloadduct **4d** (Scheme 2; see later section for characterization), which decomposed to [(Me$_3$tacn)$_2$Ru$_2{}^{III}$(μ-O)(μ-CF$_3$CO$_2$)$_2$](ClO$_4$)$_2$ (characterized by UV−vis spectroscopy) upon standing overnight at room temperature. Complex **4d** could be extracted from the aqueous *tert*-butyl alcohol mixture to CH_2Cl_2, and the UV−vis spectrum of the CH_2Cl_2 extract displayed an intense absorption band at $\lambda_{max} = 396$ nm (Figure S4a). We found that **4d** could be kept in CH_2Cl_2 solution without significant decomposition over 14 h under ambient conditions, as manifested by <10% reduction in absorption intensity of the 396 nm band. Similar Ru(III) cycloadducts obtained by reacting **1** with other alkenes have also been characterized by UV−vis spectroscopy (Figures S5 and S6), and their spectral data collected in CH_2Cl_2 are given in Table S4.

The Ru(III) cycloadducts from the reactions of **1** with alkenes can be isolated by extraction into CH_2Cl_2 from the aqueous *tert*-butyl alcohol mixture. After column chromatography to remove excess alkene and *tert*-butyl alcohol, the complexes were recrystallized from a chloroform−hexane mixture (see Experimental Section for detail). It should be noted that complex **1** was insoluble in CH_2Cl_2, and *no effective cycloadduct formation was observed by* reacting **1** with alkenes in CH_2Cl_2. Recrystallization of the cycloadducts with an acetonitrile−diethyl ether mixture give $[(Me_3tacn)Ru^{II}(MeCN)_3](ClO_4)_2$ exclusively.

With cyclooctene as substrate, cycloadduct **4a** has been characterized by X-ray diffraction analysis (Tables S5 and S6). As depicted in Figure 2a, the *cis*-configurated O(1)−Ru−O(2) moiety is bound to the alkenic carbon atoms C(1) and C(2) to form a five-membered metallacycle. We previously reported the isolation and structural characterization of a related [3 + 2] adduct obtained from the reaction of **1** with bis(trimethylsilyl)-acetylene.[11a] It is well-known that OsO_4 reacts with alkenes to form the related osmium(VI) glycolate complexes, some of which have been characterized by X-ray crystallography.[16]

In **4a**, the ruthenium atom adopts a distorted octahedral geometry coordinating to the Me_3tacn and η^1-trifluoroacetate ligands. The bond angles around C(1) and C(2) atoms are: O(1)−C(1)−C(2) = 109.6(5)°, O(2)−C(2)−C(1) = 108.6(5)°, O(1)−C(1)−C(8) = 107.1(5)°, O(2)−C(2)−C(3) = 110.2(5)°, C(1)−C(2)−C(3) = 116.7(5)°, and C(2)−C(1)−C(8) = 117.5(6)°. The respective Ru−O(1) and Ru−O(2) distances are 2.136(4) and 1.932(4) Å; the latter distance is comparable to the related ones in $[(Me_3tacn)(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)_2O]^+$ [1.977(5) and 1.979(6) Å][11a] and $[^nBu_4N][Ru^{VI}(N)(L)]$ [1.956(3) and 1.957(3) Å; L = 1,2-bis(2-hydroxyphenyl-1-carboxamido)-benzene tetraanion],[17] and $[Ru_2(Cl_4Cat)_4]^{3-}$ complexes [1.998(2), 1.965(2), 1.990(2), and 1.973(2) Å; Cl_4Cat = tetrachlorocatecholate].[18] The relatively long Ru−O(1) distance [2.136(4) Å] is comparable to the Ru−OH_2 or Ru−O(H)R distances found in $[(Me_3tacn)(bpy)Ru^{II}(OH_2)]^{2+}$ [2.168(3) Å; bpy = 2,2′-bipyridine],[9d] $[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ [2.199(3) Å],[10f] and $[Ru^{III}(HL)Cl_2(PPh_3)]$ complexes [2.123(3) Å; H_2L = 2,6-bis-(2,2-diphenyl-2-hydroxyethyl)pyridine],[19] suggesting that the O(1) atom is protonated. Based on electrical charge balance and the measured bond distances, **4a** should correspond to a Ru(III) formulation, which concurs with the results of magnetic susceptibility measurements (see later sections).

The C(1)−O(1) and C(2)−O(2) distances are 1.477(7) and 1.433(7) Å, respectively; these values are close to the related $C(sp^3)$−O distances [1.39(2) and 1.45(2) Å] found in $[Ru^{III}(L)(PPhMe_2)_2Cl]$ [H_2L = 2,6-bis(2,2-diphenyl-2-hydroxyethyl)-pyridine].[19] The C(1)−C(2) distance [1.524(9) Å] is comparable to other C−C single bond distances (ca. 1.54 Å) of the rest of the cyclooctane ring moiety.

Similarly, cycloadduct **4b** obtained by reacting *trans*-β-methylstyrene with **1** in aqueous *tert*-butyl alcohol has also been structurally characterized (Tables S5 and S7). As shown in Figure 2b, **4b** is isostructural to **4a** with the *cis*-RuO_2 moiety bound to the two alkenic carbon atoms C(1) and C(2) to form a five-membered metallacycle.

Complexes **4a** and **4b** are paramagnetic, and their respective magnetic moments (μ_{eff}) of 1.94 and 1.99 μ_B at 298 K (Evan's method) are compatible with a low-spin d^5 ruthenium(III) ion.[10f,20]

ESI-MS Studies on the Ru(III) Cycloadducts 4. After treating **1** with cyclooctene (100 equiv) in aqueous *tert*-butyl alcohol for 10 min at room temperature (see Experimental Section), the reaction mixture was extracted with CH_2Cl_2 and the organic extract was analyzed by ESI-MS (Figure S7), which revealed two prominent cluster peaks at *m/z* 529.1 (M^+) and 415.3 ($[M - CF_3CO_2]^+$) [no cluster peak of the starting **1** (*m/z* 418) was observed]. The parent ion at *m/z* 529.1 was formulated as $[(Me_3tacn)(CF_3CO_2)Ru^{III}O(H)CH(CH_2)_6HCO]^+$ based on the isotopic distribution pattern, which is identical to that observed for an authentic complex **4a**. If the aqueous *tert*-butyl alcohol mixture was directly analyzed by ESI-MS (i.e., without prior CH_2Cl_2 extraction), $[(Me_3tacn)(CF_3CO_2)Ru(OH_2)]^+$ (*m/z* = 403.1) was found to be the most prominent species, with **4a** detected only at <5% abundance. This finding indicates that the cycloadduct is unstable in the aqueous medium, probably due to hydrolysis leading to release of the *cis*-1,2-diol product (see later section). Analogous phenomena were observed for the reactions of **1** with other alkenes (see the ESI-MS in Figures S8−S16 and Table S4).

As noted in earlier sections, oxidation of *cis*-stilbene by **1** in aqueous *tert*-butyl alcohol afforded *cis*-stilbene oxide and benzaldehyde without formation of any *syn*-dihydroxylation product. When the reaction of **1** with *cis*-stilbene was analyzed by ESI-MS, four prominent cluster peaks at *m/z* 599.1, 491.1, 413.9, and 403.2 were observed (Figure S11). The peak at *m/z* 599.1 matches the formulation of either $[(Me_3tacn)(CF_3CO_2)RuO(H)PhCHCH(Ph)O]^+$ or $[(Me_3tacn)(CF_3CO_2)Ru(OCHPhCHPh)OH]^+$ (i.e., epoxide adduct). The species at *m/z* 403.2 should correspond to $[(Me_3tacn)(CF_3CO_2)Ru(OH_2)]^+$. MS−MS analysis revealed that the peak at *m/z* 491.1, which is assignable to $[(Me_3tacn)(CF_3CO_2)Ru(PhCHO)]^+$, dervied from the parent ion at *m/z* 599.1 (probably due to loss of PhCHO). The peak at *m/z* 413.9 can be assigned to $[(Me_3tacn)(CF_3CO_2)Ru(CO)]^+$, which could arise from $[(Me_3tacn)(CF_3CO_2)Ru(PhCHO)]^+$ by losing C_6H_6.

(16) (a) Pearlstein, R. M.; Blackburn, B. K.; Davis, W. M.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 639. (b) Cartwright, B. A.; Griffith, W. P.; Schröder, M.; Skapski, A. C. *Inorg. Chim. Acta* **1981**, *53*, L129. (c) Schröder, M.; Nielson. A. J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1979**, 1607. (d) Schröder, M.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1599. (e) Cartwright, B. A.; Griffith, W. P.; Schröder, M.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1978**, 853.
(17) Chan, P.-M.; Yu, W.-Y.; Che, C.-M.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **1998**, 3183.
(18) Kondo, M.; Hamatani, M.; Kitagawa, S.; Pierpont, C. G.; Unoura, K. *J. Am. Chem. Soc.* **1998**, *120*, 455.
(19) Yip, K.-L.; Yu, W.-Y.; Chan, P.-M.; Zhu, N.-Y.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **2003**, 3556.
(20) Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 933.

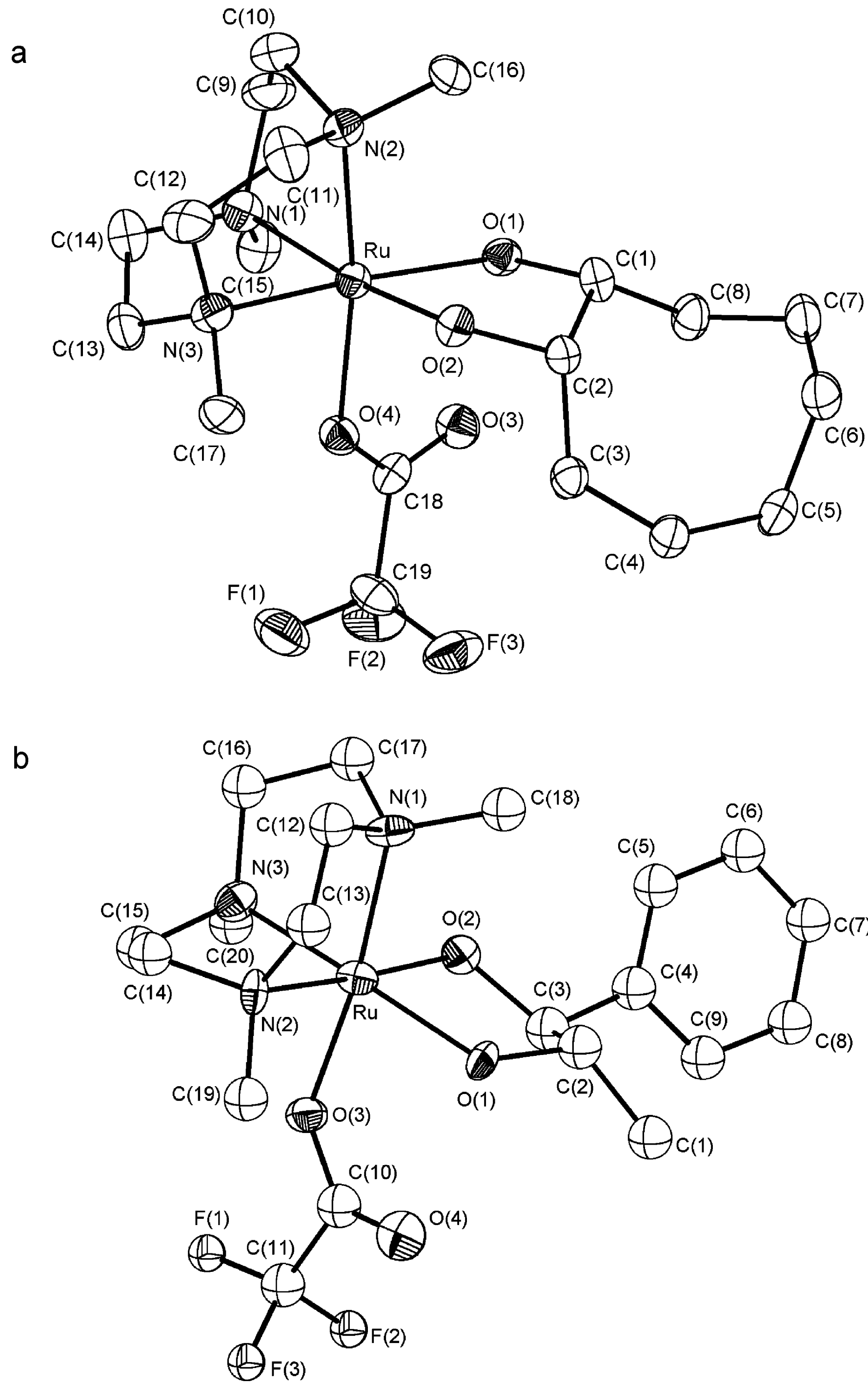


Figure 2. Perspective view of the complex cations of (a) $[(Me_3tacn)(CF_3CO_2)Ru^{III}O(H)CH(CH_2)_6HCO]ClO_4$ (**4a**) and (b) $[(Me_3tacn)(CF_3CO_2)Ru^{III}O(H)$-$PhCHCH(CH_3)O]ClO_4$ (**4b**).

Stoichiometric Oxidative Cleavage of C═C Bonds by $[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (1). In acetonitrile, oxidation of cyclooctene by **1** afforded 1,8-octanedialdehyde exclusively (Table 2, entry 1). Similar results were obtained for other cyclic alkenes (entries 3−5), and the dialdehyde products were obtained in ca. 70% yields. In all cases, $[(Me_3tacn)(CF_3CO_2)$-$Ru^{II}(MeCN)_2]ClO_4$ was produced quantitatively.

Likewise, *trans*-β-methylstyrene reacted with **1** in degassed acetonitrile to give benzaldehyde in 85% yield (Table 2, entry 6). However, the analogous *cis*-stilbene oxidation afforded *cis*-stilbene oxide in 45% yield and benzaldehyde in 32% yield (Table 2, entry 7). No *trans*-stilbene oxide was detected by ^1H NMR analysis of the crude reaction mixture.

The oxidative C═C cleavage reaction proceeded via formation of a distinct intermediate species. For example, reaction of **1** with cyclohexene in acetonitrile instantaneously produced a metastable complex **5d** featuring three broad absorption shoulders at λ_{max} = ca. 290, 360 and 420 nm (Figure S4b), a spectral profile different from that of cycloadduct **4d** in acetonitrile (λ_{max} = 396 nm). Upon standing in acetonitrile at room temperature, **5d** gradually transformed to $[(Me_3tacn)(CF_3CO_2)Ru^{II}(MeCN)_2]$-$ClO_4$ over 12 h. Spectral data for the reactions of **1** with other alkenes in acetonitrile are depicted in Table S8. Attempts to isolate the intermediates from the acetonitrile solutions by diethyl ether-induced precipitation were unsuccessful; a gummy solid was obtained in all cases. Subsequent recrystallization of the gummy solid with an acetonitrile/diethyl ether mixture gave $[(Me_3tacn)Ru^{II}(MeCN)_3](ClO_4)_2$. Interestingly, when an acetonitrile/water mixture (2:1 v/v) was employed as solvent, the reaction of **1** with cyclohexene afforded cycloadduct **4d** (as characterized by UV−vis and FAB-MS analyses).

For the reaction of **1** with cyclohexene (100 equiv) in acetonitrile, the mass spectrum of the reaction mixture containing **5d** shows two prominent peaks at *m*/*z* 501.0 and 426.9 (Figure S17). The peak at *m*/*z* 426.9 is assignable to $[(Me_3tacn)(CF_3CO_2)Ru^{II}(MeCN)]^+$, which is not a fragment of the species with *m*/*z* 501.0, as revealed by MS−MS analysis. The peak at *m*/*z* 501.0 is essentially the same as the parent ion peak of **4d**, suggesting that **5d** and **4d** are structurally related. However, the two species display different UV−vis spectra (see above), and their magnetic properties are different (see later section).

By reacting **1** with styrene in acetonitrile, the ESI-MS spectrum of the reaction mixture revealed two prominent peaks at *m*/*z* 522.9 and 426.9 (Figure S18). The peak at *m*/*z* 522.9 matches the parent molecular ion of **5f**. Similar ESI-MS results were observed for other alkenes. In all cases, the molecular ion corresponding to the starting ruthenium oxidant was not observed.

Kinetic Studies on the [3 + 2] Cycloaddition of $[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (1) with Alkenes in Acetonitrile. Reaction of styrene (50-fold excess) with **1** in acetonitrile at 278 K produced a spontaneous UV−vis spectral change (Figure S19). The first 18 s of the reaction was characterized by the disappearance of the 330 nm band with a concomitant formation of a broad shoulder band at ca. 420 nm. No further significant spectral change (at 278 K) has been observed for an additional 3 min after mixing. For the analogous cyclohexene oxidation conducted in acetonitrile (278 K), similar spectral changes were observed (Figure S20). During the time period of 0−21 s, the UV−vis spectral changes were featured by reduction of the 330 nm band, accompanied by the emergence of a shoulder band at ca. 420 nm.

Although **1** was unstable in aqueous *tert*-butyl alcohol at room temperature, a much higher stability was observed in acetonitrile, which was manifested by <10% spectral change over 3 h in the absence of alkene substrates. Thus, the slow self-decomposition of **1** would not interfere with the kinetics of the cycloaddition reactions conducted in acetonitrile.

The kinetics of the cycloaddition reaction with a series of alkenes in acetonitrile at 298 K has been studied by stopped-flow spectrophotometry. By monitoring the increase in the absorbance at $\lambda_{max} = 420$ nm (the metastable complexes **5** have higher absorption than **1** at 420 nm), the rate law $= k_2[\mathbf{1}][\text{alkene}]$ (k_2 = second-order rate constant) was established. In the presence of 20- to 100-fold excess alkene, a first-order kinetics was obtained (Figure S21). The pseudo-first-order rate constants (k_{obs}) were evaluated by the nonlinear least-squares fits of the growth curves, and the slopes of the k_{obs} vs [alkene] plots gave the k_2 values. The results are listed in Table 3. Under the concentrations employed in this work, no rate saturation was observed.

The temperature dependence of the k_2 values for the reactions of **1** with styrene, cyclooctene, cyclohexene, and *trans*-β-(trimethylsilyl)styrene has been examined (Table S9). The activation parameters were determined from the $\ln(k_2/T)$ vs $1/T$ plots, which are linear over the temperature range studied (293−315 K) (Figures S22−S25). The entropies of activation ($\Delta S^\ddagger$) are -15.6 ± 1.2, -10.4 ± 1.6, -9.5 ± 0.7, and -11.6 ± 1.8 cal mol^{-1} K^{-1}, and the enthalpies of activation ($\Delta H^\ddagger$) are 10.3 ± 0.4, 10.3 ± 0.5, 11.4 ± 0.2, and 11.9 ± 0.6 kcal mol^{-1}, respectively, for the oxidations of styrene, cyclooctene, cyclohexene, and *trans*-β-(trimethylsilyl)styrene (Table S10). The observed $\Delta S^\ddagger$ and $\Delta H^\ddagger$ values are comparable to the analogous reactions between **1** and some disubstituted alkynes[11a] (Table S10). The large and negative $\Delta S^\ddagger$ values are consistent with rate-limiting association of **1** and alkenes.

Discussion

Alkene *cis*-dihydroxylation by OsO_4 is a synthetically important reaction.[2] The mechanism of the OsO_4-mediated alkene *cis*-dihydroxylation has been a subject of extensive experimental[21] and theoretical investigations.[22] According to the literature,[2,21,22] major controversy revolves around two mechanistic deliberations: (1) concerted [3 + 2] cycloaddition and (2) nonconcerted metallaoxetane pathways[23] (Scheme S1). Compared to OsO_4, the reaction of RuO_4 with alkenes received less attention. RuO_4 is a stronger oxidant than OsO_4, and it readily oxidizes alkenes resulting in C═C bond cleavage.[12] The reaction of RuO_4 with alkenes was believed to proceed via a cyclic Ru(VI) diester intermediate, which subsequently decomposes to give the C═C bond cleavage products.[24] Previously, Sica and co-workers[24] reported the isolation and spectroscopic characterization of the cyclic Ru diester complex from the reaction of RuO_4 with alkenes.

In this work, the structurally characterized $[(Me_3tacn)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**) underwent alkene *cis*-dihydroxylation and oxidative C═C bond cleavage with alkenes depending on the reaction medium employed. In aqueous *tert*-butyl alcohol, oxidation of alkenes by **1** gave *cis*-1,2-diols in good yields, whereas oxidative C═C bond cleavage reaction prevailed in nonaqueous medium (e.g., acetonitrile). The reaction in *aqueous*

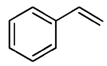
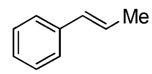
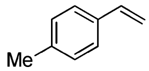
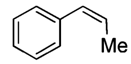
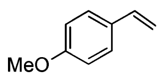
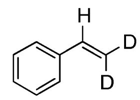
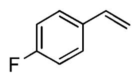
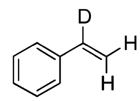
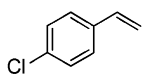
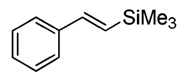
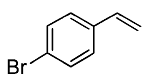
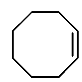
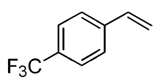
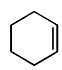
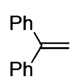
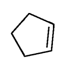
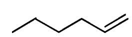
(21) (a) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 11038. (b) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 319. (c) Norrby, P.-O.; Kolb, H. C.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 8470. (d) Corey, E. J.; Noe, M. C.; Sarshar, S. *Tetrahedron Lett.* **1994**, *35*, 2861. (e) Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 12579. (f) Corey, E. J.; Noe, M. C.; Sarshar, S. *J. Am. Chem. Soc.* **1993**, *115*, 3828. (g) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263. (h) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628. (i) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(22) (a) Frunzke, J.; Loschen, C.; Frenking, G. *J. Am. Chem. Soc.* **2004**, *126*, 3642. (b) Deubel, D. V.; Frenking, G. *Acc. Chem. Res.* **2003**, *36*, 645. (c) Deubel, D. V.; Schlecht, S.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 10085. (d) Norrby, P.-O.; Rasmussen, T.; Haller, J.; Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 10186. (e) Ujaque, G.; Maseras, F.; Lledós, A. *J. Am. Chem. Soc.* **1999**, *121*, 1317. (f) Torrent, M.; Deng, L.; Duran, M.; Sola, M.; Ziegler, T. *Organometallics* **1997**, *16*, 13. (g) DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907. (h) Dapprich, S.; Ujaque, G.; Maseras, F.; Lledós, A.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1996**, *118*, 11660. (i) Norrby, P.-O.; Kolb, H. C.; Sharpless, K. B. *Organometallics* **1994**, *13*, 344.

(23) For recent works on isolation of metallaoxetane complexes, see: (a) Szuromi, E.; Shan, H.; Sharp, P. R. *J. Am. Chem. Soc.* **2003**, *125*, 10522. (b) Flood, T. C.; Iimura, M.; Perotti, J. M.; Rheingold, A. L.; Concolino, T. E. *Chem. Commun.* **2000**, 1681. For a review on metallaoxetanes, see: (c) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* **1990**, *90*, 1483.

(24) Albarella, L.; Giordano, F.; Lasalvia, M.; Piccialli, V.; Sica, D. *Tetrahedron Lett.* **1995**, *36*, 5267.

Table 3. Second-Order Rate Constants (k_2) for the Oxidation of Alkenes by **1** in Acetonitrile at 298 K[a]

entry	alkene	k_2/dm^3 mol^{-1} s^{-1}	$E_{1/2}$/V	entry	alkene	k_2/dm^3 mol^{-1} s^{-1}	$E_{1/2}$/V
1		68 ± 1	1.65	9		22 ± 1	–
2		180 ± 8	1.38	10		41 ± 2	–
3		724 ± 8	1.15	11		82 ± 3	–
4		77 ± 3	–	12		71 ± 1	–
5		102 ± 2	–	13		33 ± 2	–
6		94 ± 1	–	14		872 ± 10	2.03
7		24 ± 1	–	15		233 ± 5	1.81
8		49 ± 2	1.22	16		218 ± 4	2.19
				17		94 ± 3	2.44

[a] Ionization potentials were taken from Garrison, J. M.; Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960.

tert-butyl alcohol proceeded via formation of a metastable Ru(III) cycloadduct, $[(Me_3tacn)(CF_3CO_2)\overline{RuO(H)C_2H_2RR'O}]^+$ (**4**); with cyclooctene and *trans*-β-methylstyrene as substrates, cycloadducts **4a** and **4b** have been structurally characterized by X-ray crystallography.

In acetonitrile, **1** cleaved the C═C bond of alkenes to give carbonyl products in up to 90% yields. Based on UV−vis and ESI-MS studies, the C═C bond cleavage reactions involved formation of the metastable complexes **5**, which are diamagnetic and displayed well-resolved NMR signals.

^{19}F NMR spectroscopy was employed to follow the oxidative C═C bond cleavage reaction. At room temperature, **1** (40 μmol) exhibited a sharp singlet peak at δ_F −75.82 ppm in CD_3CN (Figure S26). After addition of cyclohexene (400 μmol), the δ_F −75.82 ppm peak of **1** was immediately replaced by a new sharp singlet signal at δ_F −76.24 ppm corresponding to the formation of **5d**. $[(Me_3tacn)(CF_3CO_2)Ru^{III}\overline{O(H)CH(CH_2)_4HCO}]^+$ (**4d**) should not be the immediate product of the reaction of **1** with cyclohexene in acetonitrile, since an authentic sample of **4d** shows a broad singlet peak at δ_F −74.15 ppm (Figure S27) under identical conditions. With reference to $[(Me_3tacn)(CF_3CO_2)Ru^{IV}\text{-}\overline{OC_2(SiMe_3)_2O}]^+$ that shows a sharp singlet signal at δ_F −76.67 ppm (Figure S28), we assign **5d** (δ_F −76.24 ppm) to a Ru(IV) species, formulated as $[(Me_3tacn)(CF_3CO_2)Ru^{IV}\overline{OCH(CH_2)_4\text{-}HCO}]^+$. Similar ^{19}F NMR results were obtained for the analogous reactions with other alkenes.

As noted in earlier sections, the Ru(IV) cycloadducts such as **5d** would gradually convert to $[(Me_3tacn)(CF_3CO_2)Ru^{II}\text{-}(MeCN)_2]ClO_4$ upon standing in acetonitrile. The ^{19}F NMR spectrum of $[(Me_3tacn)(CF_3CO_2)Ru^{II}(MeCN)_2]ClO_4$ shows a sharp singlet at δ_F −76.18 ppm (Figure S29), which overlaps with the ^{19}F signal of **5d**. Interestingly, continuous monitoring of the Ru(IV) cycloadduct in purified d_3-acetonitrile (alcohol free) at room temperature over an additional 12 h did not reveal any broad signal at δ_F = −74.15 ppm corresponding to a Ru(III) complex formulation (i.e., **4d**).

Combining the results from the UV−vis, ESI-MS, and NMR studies, we conclude that in acetonitrile **1** reacted with alkenes to give a [3 + 2] Ru(IV) cycloadduct, which subsequently underwent C═C bond cleavage to form dialdehydes at a longer time scale. In the presence of water (e.g., aqueous *tert*-butyl alcohol), the Ru(IV) cycloadduct would undergo hydrolysis to release the chelated glycolate as *cis*-diols. Or, this process would be preceded by reduction with protonation on one of the Ru−O bonds to give the Ru(III) cycloadduct.

Transition State of the [3 + 2] Cycloaddition. When the log k_2 values (Table 3) are plotted against the $E_{1/2}$ values for one-electron oxidation of alkenes, no linear free energy relationship can be established (Figure S30). For the alkenes studied in this work, the k_2 values vary by about 18 times despite an overall span of 1.3 V in the $E_{1/2}$ values. Except for 1,1-diphenylethylene and cyclooctene, alkenes with lower one-electron oxidation potentials are more reactive. The reaction of 1,1-diphenylethylene ($E_{1/2}$ = 1.22 V vs SCE) with **1** is 15 times slower than that of 4-vinylanisole ($E_{1/2}$ = 1.15 V vs SCE) despite that these two alkenes have comparable one-electron oxidation potentials. We reason that steric effect could be an additional factor affecting the cycloadditions between *cis*-dioxoruthenium(VI) and alkenes. As depicted in Table 3, aliphatic alkenes are more reactive than styrenes regardless of the higher $E_{1/2}$ values by up to 1 V for the former. This is readily seen by comparing the k_2 values of styrene (68 ± 1 $dm^3\ mol^{-1}\ s^{-1}$), cyclohexene (233 ± 5 $dm^3\ mol^{-1}\ s^{-1}$), cyclooctene (872 ± 10 $dm^3\ mol^{-1}\ s^{-1}$), cyclopentene (218 ± 4 $dm^3\ mol^{-1}\ s^{-1}$) and 1-hexene (94 ± 3 $dm^3\ mol^{-1}\ s^{-1}$).

The absence of a linear free-energy relationship between log k_2 and $E_{1/2}$ (one-electron oxidation potential) and the modest dependence of the k_2 values upon the $E_{1/2}$ values of alkenes observed for the cycloaddition reaction between **1** and alkenes are incompatible with a mechanism involving a rate-limiting single electron transfer reaction. For a reaction involving rate-limiting single electron transfer, the slope of the log k_2 vs ΔG plot (ΔG = driving force of the reaction) would be equal to $-16.8\ eV^{-1}$;[25] therefore, lowering the $E_{1/2}$ value of alkenes by 1 V should cause a dramatic rate acceleration.

Concerted versus Nonconcerted Mechanism. The stereoselectivity of *cis*-alkene oxidation could be taken as a measure for the concertedness of oxo-transfer reactions from oxo-metal oxidants.[26] In literature, the OsO_4-mediated syn-dihydroxylation of *cis*-2-butene-1,4-diacetate is known to afford 1,4-di-*O*-acetylerythritol with excellent *cis*-stereoretention,[27] and a concerted [3 + 2] pathway (Scheme S1, path A) was previously proposed.[21a,b,22g,h] In this work, we observed similar *cis*-stereoselectivity for the dihydroxylation of *cis*-2-butene-1,4-diacetate by **1** in aqueous *tert*-butyl alcohol, and 1,4-di-*O*-acetylerythritol was obtained in 75% yield (Table 1, entry 8). The anti-dihydroxylation product, i.e., 1,4-di-*O*-acetylthreitol, was not detected by NMR analysis of the crude reaction mixture. Under similar conditions, *cis*-β-methylstyrene reacted with **1** to afford *erythro*-1-phenyl-1,2-propanediol in 84% yield, no anti-dihydroxylation product was detected.

The reactions of *cis*-stilbene with **1** in both aqueous *tert*-butyl alcohol and acetonitrile have also been examined. *cis*-Stilbene oxide (58% yield) and benzaldehyde (35% yield) were found, and no *trans*-stilbene oxide was detected. The observed stereoselectivity is comparable to the analogous reactions when *trans*-dioxoruthenium(VI) porphyrins[10] and oxo-ruthenium(IV) complexes containing polypyridine ligands[9b,c] were used as oxidants.

The synchronicity of the C−O bond formation has been examined by measuring the secondary kinetic isotope effect (KIE). A concerted reaction pathway involving synchronous C−O bond formation would require a simultaneous rehybridization of the alkenic α- and β-carbon atoms from sp^2 to sp^3 in the rate-determining step, resulting in similar inverse secondary KIE for the α- and β-carbon atoms. In this work, the k_H/k_D value was found to be 0.96 ± 0.03 for α-deuteriostyrene (entries 1 and 12, Table 3) and 0.83 ± 0.04 for β-d_2-styrene (entries 1 and 11, Table 3), with the secondary KIE per deuterium in the latter case being 0.92 ± 0.02. Such secondary KIE results are comparable to those reported for the OsO_4-mediated *cis*-dihydroxylation reaction, which exhibits secondary KIEs (k_H/k_D per deuterium) of 0.91 and 0.93 for C_α and C_β atoms of alkenes, respectively, and is proposed to proceed by a synchronous transition state involving formation of two C−O bonds.[22g] For comparison, the epoxidation of *cis*-β-deuteriostyrene catalyzed by chiral Mn(salen) complexes (which proceeds by a stepwise pathway) has k_H/k_D values of 0.82−0.95.[28]

Metallaoxetane Formation by [2 + 2] Pathway. Alternative to the [3 + 2] pathway, a stepwise reaction pathway involving a metallaoxetane formation by a [2 + 2] addition of C═C bond across an Os═O bond (Scheme S1, path B) was previously proposed in the literature.[21c,g−i] Indeed, d^0 oxo-titanium and -zirconium(V) complexes are known to react with the C≡C bond of alkynes to give metallaoxetene complexes.[29]

For a [2 + 2] pathway, the presence of a vacant coordination site is desirable. If metallaoxetane formation is obligatory for the reactions of alkenes with *cis*-dioxoruthenium(VI), the coordinatively saturated *cis*-[(Tet-Me_6)$Ru^{VI}O_2$](ClO_4)$_2$ (**2**) would be ineffective for alkene oxidation since a highly energetic seven-coordinate ruthenium site would have to be formed. However, **2** could effectively oxidize cyclooctene in aqueous *tert*-butyl alcohol to furnish the *cis*-1,2-diol and 1,8-octanedialdehyde in 22% and 60% yield, respectively. Therefore, a rate-limiting [2 + 2] pathway appears implausible for reaction of *cis*-dioxoruthenium(VI) with alkenes.

Hammett Correlation Studies. The effect of *para*-substituents on the reactions of substituted styrenes ($YC_6H_4CH{=}CH_2$) with **1** has been examined; and the k_2 values are in the order Y = OMe > Me > Cl > Br > F > H > CF_3. Fitting (by the least-squares method) the log k_{rel} with Hammett σ^+ constants gave a straight line (R = 0.96) with a ρ^+ value of −1.05 (Figure S31). This finding is different from the previous works on styrene oxidation by OsO_4[30] and $^nBu_4N[MnO_4]$,[31] in which cases

(25) (a) Rehm, D.; Weller, A. *Isr. J. Chem*. **1970**, *8*, 259. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.
(26) Ostovic, D.; Bruice, T. C. *Acc. Chem. Res.* **1992**, *25*, 314.
(27) Milas, N. A.; Sussman, S.; Mason, H. S. *J. Am. Chem. Soc.* **1939**, *61*, 1844.
(28) Palucki, M.; Finney, N. S.; Pospisil, P. J.; Güler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948.
(29) (a) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (b) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (c) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753.
(30) Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H.-L.; McGrath, D. V.; Rubin, A. E.; Norrby, P.-O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840.
(31) Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

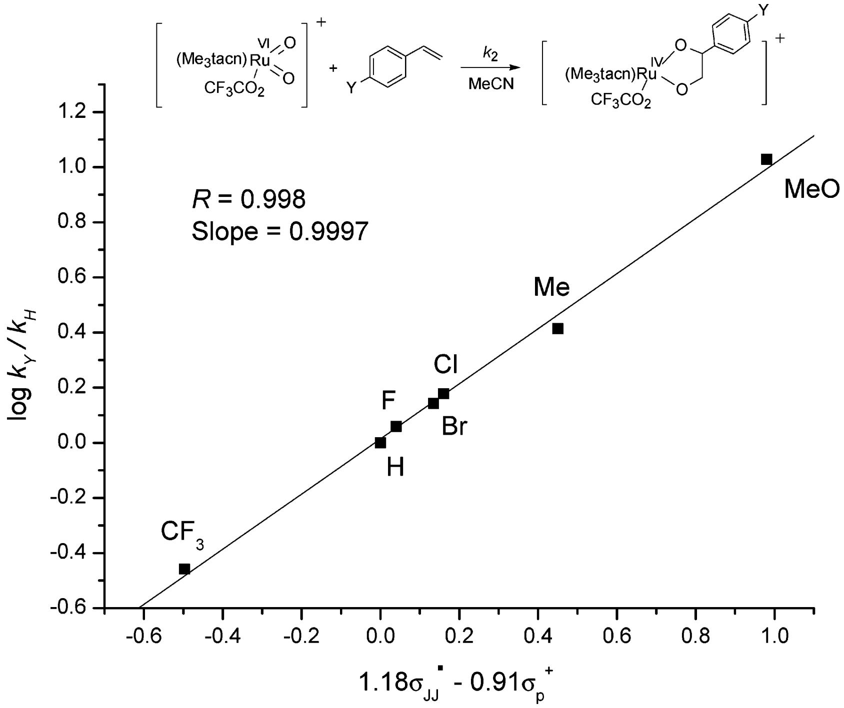


Figure 3. Dual-parameter Hammett plot for the oxidation of *para*-substituted styrene by **1** at 298 K ($k_{rel} = k_Y/k_H$).

concave free energy plots were obtained. The small and negative ρ^+ value indicates little positive charge development at the α-carbon atom. It should be noted that bromination ($\rho^+ = -4.1$)[32] and hydration ($\rho^+ = -3.5$)[33] of alkenes involving rate-limiting formation of carbocation are associated with large and negative ρ^+ values.

A dual-parameter Hammett correlation [log k_{rel} vs (σ_p^+, $\sigma_{JJ}^{\bullet}$)[34]], which takes into account the spin delocalization effect, for the reactions of $YC_6H_4CH{=}CH_2$ with **1** gave a better straight line (log $k_{rel} = 1.18\sigma_{JJ}^{\bullet} - 0.91\sigma_p^+$, $R = 0.998$, slope = 1.00) (Figure 3) than the log k_{rel} vs σ^+ correlation. This might imply the development of some radical character at the α-carbon in the transition state.

On the basis of kinetic studies and product analysis, we propose that **1** reacts with alkenes by a formal [3 + 2] cycloaddition (Scheme 3).[35] These cycloaddition reactions possibly proceed through a concerted pathway, or through a stepwise pathway involving rate-limiting formation of a carbon-centered radical intermediate. The stereoselectivity of *cis*-alkene oxidation by **1**, coupled with the KIE results, favors the concerted mechanism.[36,37] In aqueous *tert*-butyl alcohol, the Ru(IV) cycloadduct would undergo further reduction to Ru(III). Hydrolysis of the Ru(III) cyclic *syn*-diolate releases the *cis*-1,2-diol products, with concomitant formation of $[(Me_3\text{-tacn})_2Ru_2^{III}(\mu\text{-}O)(\mu\text{-}CF_3CO_2)_2](ClO_4)_2$. In acetonitrile, the Ru(IV) cycloadducts preferentially undergo C−C bond cleavage leading to production of carbonyl compounds.

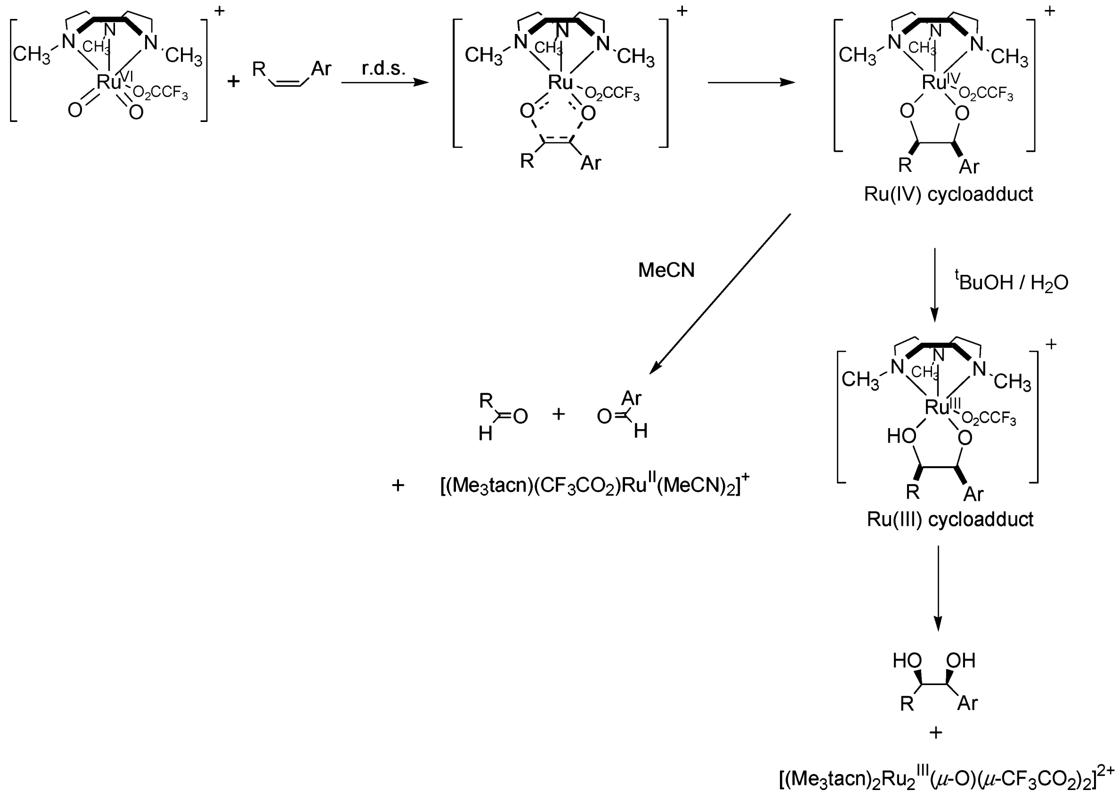
In conclusion, we present that a structurally characterized *cis*-dioxoruthenium(VI) complex **1** can effect alkene *cis*-dihydroxylation and oxidative C=C bond cleavage reactions, both involving direct interaction of the two oxo ligands with C=C bond. Prompted by the recent works of Que and co-workers that structurally related iron complexes are active catalysts for alkene dihydroxylations,[3a−c] our preliminary results showed that $[(Me_3tacn)(CF_3CO_2)_2Ru^{III}(OH_2)]CF_3CO_2$ can catalyze alkene dihydroxylation using aqueous H_2O_2 as a terminal oxidant. For example, treating cyclooctene with 35% aqueous H_2O_2 and $[(Me_3tacn)(CF_3CO_2)_2Ru^{III}(OH_2)]CF_3CO_2$ (1 mol %) in aqueous *tert*-butyl alcohol produced *cis*-1,2-cyclooctanediol and cyclooctene oxide in 50% and 42% yields with 100% alkene consumption. More studies of this catalytic reaction are underway.

Experimental Section

Stoichiometric Alkene *cis*-Dihydroxylation by 1. To a 100-mL Schlenk flask were added alkene (30 mmol), *tert*-butyl alcohol (10 mL), and distilled water (2 mL). The mixture was degassed by three freeze−pump−thaw cycles and filled with argon. Upon addition of **1** (300 μmol) under a positive pressure of argon, the reaction mixture was stirred magnetically for at least 14 h to give a deep purple solution. The organic products were extracted with diethyl ether (3 × 50 mL).

(32) Yates, K.; McDonald, R. S.; Shapiro, S. A. *J. Org. Chem.* **1973**, *38*, 2460.
(33) Schubert, W. M.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559.
(34) Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283.
(35) Given the formation of *cis*-stilbene oxide in the reaction of **1** with *cis*-stilbene (entry 10, Table 1), another dihydroxylation mechanism to be considered is epoxidation followed by ring expansion. However, this mechanism is incompatible with the stereoselectivity of the *cis*-alkene oxidation reactions. If epoxidation followed by ring expansion is involved, *trans*-dihydroxylation products should be formed predominantly. For example, treatment of *cis*-β-methylstyrene oxide with **3** under comparable conditions afforded *trans*-dihydroxylation product in 99% yield with 85% conversion.
(36) We found that *cis*- and *trans*-diol products are stable under the reaction conditions. For example, treatment of a 1:1 mixture of *threo*- and *erythro*-1,2-diphenyl-ethane-1,2-diol with **3** under comparable conditions to those of the *cis*-dihydroxylation reactions resulted in neither formation of benzaldehyde nor change of the ratio of the *threo*- vs *erythro*-diol, as shown by GC or ^{1}H NMR analysis. Therefore, the observed stereoselectivity of the *cis*-alkene oxidation by **1** is unlikely to arise from a sufficiently more rapid reaction of the *trans*-dihydroxylation product than the *cis*-counterpart.
(37) As pointed by a reviewer, if the reaction proceeded through a stepwise pathway involving rate-limiting formation of a carbon-centered radical intermediate, the k_H/k_D value for α-deuteriostyrene should be larger than 1.00. See for example: (a) Olson, L. P.; Niwayama, S.; Yoo, H.-Y.; Houk, K. N.; Harris, N. J.; Gajewski, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 886. (b) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385.

Scheme 3. Proposed General Mechanism for the Aromatic Alkene Oxidations by **1**



After washing with brine (2 × 10 mL), the combined organic extracts were dried over $MgSO_4$. By rotary evaporation, the ethereal extract was concentrated to ca. 3 mL, and the residue mixture was loaded onto a silica gel column for chromatographic purification using a hexanes−ethyl acetate mixture as eluant. The organic products (*cis*/*trans*-diols, carbonyl compounds) were identified by ^{1}H and ^{13}C NMR spectroscopy with reference to authentic or literature data.

For isolation of $[(Me_3tacn)_2Ru_2^{III}(\mu\text{-O})(\mu\text{-CF}_3CO_2)_2](ClO_4)_2$ (**3**), addition of a saturated $NaClO_4$ solution to the aqueous layer afforded a deep purple solid, which was recrystallized in an acetone/diethyl ether mixture (acetone/diethyl ether = 1:10 v/v). UV−vis (H_2O): λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1}): 261 (11600), 545 (7300). FAB-MS: *m*/*z* 394 (M^{2+}), 787 (M^+), 887 ($[M + ClO_4)^+]$). Anal. Calcd for $C_{22}H_{42}N_6O_{13}F_6Cl_2Ru_2$ (%): C, 26.81; H, 4.3; N, 8.53. Found: C, 27.13; H, 4.11; N, 8.32.

Caution! Transition metal perchlorates are potentially explosive, and particular care should be exercised in preparation and handling.

Stoichiometric Oxidative Cleavage of Alkenes by 1. A similar procedure to the *cis*-dihydroxylation reactions was employed, except that acetonitrile was used as solvent.

Isolation of Ru(III) Cycloadducts. Alkene (30 mmol) was added to a Schlenk flask (100 mL) containing *tert*-butyl alcohol/acetonitrile (10 mL) and water (2 mL). Upon degassing the mixture by three freeze−pump−thaw cycles, **1** (300 μmol) was added under a positive pressure of argon. After stirring for 10 min, a clear yellow solution was obtained. The aqueous *tert*-butyl alcohol solution was extracted with CH_2Cl_2 (2 × 30 mL), and the CH_2Cl_2 extract was dried over $MgSO_4$. Removal of $MgSO_4$ by filtration, followed by addition of hexane (400 mL) to the filtrate with vigorous stirring, gave a clear light yellow solution. The solution mixture was passed through a silica gel column [ca. 4 cm (diameter) × 1 cm (height)] topped with a similar amount of acid-washed sand with the aid vacuum being applied at the outlet. The silica gel column was then washed with hexane (500 mL) to remove the residual alkene/*tert*-butyl alcohol. The cycloadduct complex adsorbed on the silica gel column was eluted with acetone (500 mL) as a yellow band. Removal of the acetone by rotary evaporation at room temperature gave a blue-green residue, which was extracted with dry $CHCl_3$ (5 mL) to give a light yellow solution. The $CHCl_3$ extract was layered with hexane, and the mixture was kept in a freezer (−20 °C) for several days. The cycloadduct complex was obtained as a yellow crystalline solid (<5% yield), which was stable in an inert atmosphere and at low temperature (−20 °C) for a few days.

ESI-MS Studies for Alkene *cis*-Dihydroxylation by 1. A mixture containing alkene (0.2 mmol), *tert*-butyl alcohol (5 mL), and water (1 mL) in a Schlenk flask was degassed by three freeze−pump−thaw cycles. Upon addition of **1** (2 μmol) under a positive pressure of argon, the mixture was stirred vigorously for 10 min to give a yellow solution, which was then treated with CH_2Cl_2 (20 mL). The yellow CH_2Cl_2 layer was separated and dried over $MgSO_4$. After filtration, aliquots of the yellow solution were taken for analysis by ESI-MS. The mass spectra were obtained after an average of 20 collective scans. Electrospray ionization mass spectra were acquired with a Finnigan MAT LCQ spectrometer. The sheath (compressed air) and auxiliary (nitrogen) gases were operated at 100 and 40 psi, respectively. Typical operating voltages were 3.0 V for capillary voltage and 3.5 kV for spray voltage. All the spectra were collected at 180 °C capillary temperature.

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Supporting Information Available: Details on materials, instrumentation, and procedures for kinetic studies; spectral and structural characterization data of complexes **3** and **4**, Figures S1−S31, Scheme S1, Tables S1−S10 and CIF files for the crystal structures of **3**, **4a** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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