Stoichiometric and Catalytic Oxidations of Alkanes and Alcohols Mediated by Highly Oxidizing Ruthenium−Oxo Complexes Bearing 6,6′-Dichloro-2,2′-bipyridine

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Received July 6, 2000

The ruthenium(II) complex *cis*-$\mathrm{[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2}$ (**1**) is a robust catalyst for C−H bond oxidations of hydrocarbons, including linear alkanes, using *tert*-butyl hydroperoxide (TBHP) as terminal oxidant. Alcohols can be oxidized by the "**1** + TBHP" protocol to the corresponding aldehydes/ketones with high product yields at ambient temperature. Oxidation of **1** with $\mathrm{Ce^{IV}}$ in aqueous solution affords *cis*-$\mathrm{[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}}$, which is isolated as a green/yellow perchlorate salt (**2**). Complex **2** is a powerful stoichiometric oxidant for cycloalkane oxidations under mild conditions. Oxidation of *cis*-decalin is highly stereoretentive; *cis*-decalinol is obtained in high yield, and formation of *trans*-decalinol is not observed. Mechanistic studies showing a large primary kinetic isotope effect suggest a hydrogen-atom abstraction pathway. The relative reactivities of cycloalkanes toward oxidation by **2** have been examined through competitive experiments, and comparisons with Gif-type processes are presented.

Introduction

Highly oxidizing metal−oxo (M=O) complexes are usually invoked as reactive intermediates in biological oxidations[1] and in Gif chemistry,[2] but literature examples of isolable M=O complexes with well-defined structural and redox properties and the ability to oxidize saturated hydrocarbons at room temperature are sparse.[3−7] Regarding the ongoing controversy surrounding the reaction mechanism of Gif-type oxidations, pathways involving $\mathrm{[Fe^{V}{=}O]}$ species and oxygenated free radicals have both been proposed.[2,8] It is difficult to differentiate these two mechanistic possibilities, partly because there is a dearth of reports describing the relative reactivities of discrete metal−oxo complexes toward different saturated C−H bonds.

In our endeavor to develop new metal catalysts for hydrocarbon functionalization, we deemed that mechanistic information on the reactivities of highly oxidizing M=O complexes toward different alkanes were important. We have previously described the preparation of high-valent ruthenium−oxo complexes supported by the 6,6′-dichloro-2,2′-bipyridine (6,6′-$\mathrm{Cl_2}$bpy) ligand.[9,10] We now report in detail on the reactivity of a *cis*-dioxoruthenium(VI) complex containing the 6,6′-$\mathrm{Cl_2}$bpy ligand toward stoichiometric alkane oxidations. In particular, the observed relative reactivities with various cycloalkanes are compared with the results previously disclosed for Gif oxidations. The catalytic activities of the Ru(II) derivative *cis*-$\mathrm{[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}}$ in organic oxidations with *tert*-butyl hydroperoxide (TBHP) as terminal oxidant are also presented.[11]

Results and Discussion

Preparation and Characterization of Ruthenium Complexes. Treatment of *cis*-$\mathrm{[Ru^{II}(6,6'\text{-}Cl_2bpy)_2Cl_2]\cdot 2H_2O}$ with $\mathrm{AgCF_3SO_3}$ in $\mathrm{H_2O}$ yielded *cis*-$\mathrm{[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2}$ (**1**) as a deep red solid in 70% yield. At ambient temperature, complex **1** is stable in solution and as a solid for over 5 days. The UV−vis spectrum of **1** in $\mathrm{H_2O}$ displays an intense absorption band at 494 nm,

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(1) *Cytochrome P-450: Structure, Mechanism and Biochemistry*, 2nd ed.; Oritz de Montellano, P. R., Ed.; Plenum Press: New York, 1995.

(2) (a) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504. (b) Barton, D. H. R. *Chem. Soc. Rev.* **1996**, *25*, 237. (c) Barton, D. H. R. *Tetrahedron* **1998**, *54*, 5805.

(3) (a) Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179. (b) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Org. Chem.* **1992**, *57*, 5523. (c) Bailey, A. J.; Griffith, W. P.; Savage, P. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3537.

(4) Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 2424.

(5) (a) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441. (b) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7139.

(6) (a) Che, C. M.; Tang, W. T.; Wong, W. T.; Lai, T. F. *J. Am. Chem. Soc.* **1989**, *111*, 9048. (b) Che, C. M.; Yam, V. W. W.; Mak, T. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2284. (c) Ho, C.; Lau, T. C.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1991**, 1259.

(7) (a) Dovletoglou, A.; Adeyemi, S. A.; Lynn, M. H.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8989. (b) Lau, T. C.; Mak, C. K. *J. Chem. Soc., Chem. Commun.* **1995**, 943. (c) Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961. (d) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(8) (a) Perkins, M. J. *Chem. Soc. Rev.* **1996**, *25*, 229. (b) Newcomb, M.; Simakov, P. A. *Tetrahedron Lett.* **1998**, *39*, 965.

(9) (a) Che, C. M.; Leung, W. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1376. (b) Che, C. M.; Lee, W. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1406. (c) Lau, T. C.; Che, C. M.; Lee, W. O.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1988**, 1406.

(10) Che, C. M.; Ho, C.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1901.

(11) Examples of metal complex/TBHP systems: (a) Conte, V.; Di Furia, F.; Modena, G. In *Organic Peroxides*; Ando, W., Ed.; John Wiley and Sons: New York, 1992; p 559. (b) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 103. (c) Kojima, T.; Matsuo, H.; Matsuda, Y. *Inorg. Chim. Acta* **2000**, *300−302*, 661 and references therein.

10.1021/jo0010126 CCC: $19.00

which can be assigned to the $d\pi(Ru) \rightarrow \pi^*(6,6'\text{-}Cl_2bpy)$ MLCT transition. The electrochemistry of **1** in aqueous solution has been studied previously.[12] The cyclic voltammogram in pH 1.0 (0.1 M CF_3CO_2H) displays two quasireversible couples at 0.93 and 1.17 V vs SCE, which were assigned as Ru(IV)/Ru(II) and Ru(VI)/Ru(IV), respectively. The cis configuration and a distorted octahedral environment around the ruthenium atom in **1** were confirmed by X-ray crystallography (see Supporting Information). The average Ru−O distance of 2.128 Å is comparable to that in $[Ru^{II}(H_2O)_6](C_7H_7SO_3)_2$ (2.122(16) Å).[13] The mean Ru−N distance of 2.055 Å is partially shorter than the analogous distances of 2.076(2) and 2.090(3) Å in *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(CH_3CN)_2](ClO_4)_2$;[14] CH_3CN is a stronger π-acid ligand than H_2O, and thus the bis(acetonitrile) complex presumably engages in weaker Ru → diimine back-bonding.

Oxidation of **1** by Ce(IV) in aqueous $NaClO_4$ solution at 0 °C gave *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2](ClO_4)_2$ (**2**) as a green/yellow solid in 60% yield. We have previously reported the synthesis of **2** from *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](ClO_4)_2$,[12] so only a brief description of its properties is given here. Complex **2** is stable for 1−2 h in the solid state at 0 °C; complete conversion to $[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(CH_3CN)_2]^{2+}$ readily occurs in acetonitrile within 1 h at room temperature. As expected from its formulation, the cyclic voltammogram of **2** measured in 0.1 M CF_3CO_2H is identical to that for **1**. Complex **2** exhibits two infrared bands at 846 and 860 cm^{-1} with different intensities, and these are tentatively assigned to the asymmetric and symmetric Ru═O stretching frequencies respectively in a *cis* geometry. Similar IR spectral data have been reported for related *cis*-dioxoruthenium(VI) complexes, namely *cis*-$[Ru^{VI}(2,2,2\text{-tet-}Me_6)_2O_2](ClO_4)_2$ (859 and 874 cm^{-1}, 2,2,2-tet-Me_6 = *N*,*N*,*N′*,*N′*-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine)[15] and *cis*-$[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]ClO_4$ (842 and 856 cm^{-1}, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[16] which have been characterized by X-ray crystallography. The UV−vis spectrum of **2** in distilled water is featureless in the visible region, but a rapid and quantitative conversion to *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ is observed upon addition of an organic reductant such as benzyl alcohol.

Stoichiometric Oxidations by *cis*-[Ru(6,6′-Cl₂bpy)₂O₂](ClO₄)₂ (2). Complex **2** has a $E°$ value of 1.17 V vs SCE, and is one of the most oxidizing ruthenium−oxo complexes to be isolated in solid form.[17] A freshly prepared sample of **2** is a powerful oxidant for various organic substrates including saturated hydrocarbons. The results of stoichiometric oxidations in acetonitrile at 298 K are summarized in Table 1. Control experiments in the absence of the ruthenium complex showed that oxidation of the organic substrates did not occur. Oxidation of cyclohexene occurred exclusively at the allylic C−H bond (entry 2), a feature which is typical for related oxoruthenium complexes including *cis*-$[Ru^{VI}(2,2,2\text{-tet-}Me_6)O_2]^{2+}$.[18] The oxidations of aryl alkenes were nonselective, so that both epoxidation and oxidative cleavage of C═C bonds were observed. The oxidations of *trans*- and *cis*-stilbene (entries 4 and 5) afforded the corresponding stilbene oxide with high stereospecificity and moderate yield, although oxidative cleavage was found to be a significant pathway. The stereospecificities of these transformations are dependent upon the integrity of complex **2**; for example, reaction of *cis*-stilbene with an aged sample of **2** gave a mixture of *cis*- and *trans*-stilbene oxides.

Table 1. Stoichiometric Oxidation of Organic Substrates (100 mg) by *cis*-[Ru^{VI}(6,6′-Cl₂bpy)₂O₂](ClO₄)₂ (50 mg, 0.06 mmol) in Acetonitrile (3 mL) at Room Temperature under a N₂ Atmosphere; Reaction Time 0.5 h

entry	substrates	product(s)	yield (%)[a]
1	norbornylene	*exo*-2,3-epoxynorbornane	78
2	cyclohexene	2-cyclohexen-1-one	60
3	styrene	styrene oxide	3
		benzaldehyde	70
4	*cis*-stilbene	*cis*-stilbene oxide	7
		benzaldehyde	16
		diphenylacetaldehyde	21
5	*trans*-stilbene	*trans*-stilbene oxide	50
		benzaldehyde	18
6	cyclopentane	cyclopentanone	46
7	cyclohexane	cyclohexanone	50 (k_H/k_D[b] = 6.5)
8	cyclohexane[c]	cyclohexanone	50
		cyclohexyl chloride	0.5
9	cyclooctane	cyclooctanone	68
10	cyclodecane	cyclodecanone	75
11	methylcyclohexane	1-methylcyclohexan-1-ol	69
12	adamantane	adamantan-1-ol	75
13	*n*-hexane	−	−
14	toluene	benzaldehyde	52
15	ethyl benzene	*sec*-phenethyl alcohol	17
		acetophenone	38
16	cumene	2-phenyl-2-propanol	32
		acetophenone	36
17	*cis*-decalin	*cis*-decalinol	77
18	cyclohexanol	cyclohexanone	78
19	benzyl alcohol	benzaldehyde	73
		benzoic acid	5
20	1-hexanol	hexanal	71
21	dimethyl sulfide	dimethyl sulfoxide	68
		dimethyl sulfone	9

[a] Product yield is based on the amount of ruthenium complex used. [b] Calculated from the competitive oxidation of cyclohexane and cyclohexane-d_{12}. [c] $CH_3CN:CCl_4$ = 9:1.

An important finding in this work is the ability of **2** to oxidize unactivated saturated C−H bonds. The oxidation of cyclohexane was completed within minutes, but linear alkane substrates such as *n*-hexane did not yield any detectable oxidized products. We note that the ruthenium product after the oxidation was *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(CH_3CN)_2]^{2+}$, as indicated by the appearance of its MLCT bands at λ_{max} 301 and 445 nm in the UV−vis spectrum. Cyclohexane was oxidized to cyclohexanone exclusively (entry 7), with a primary kinetic isotope effect of 6.5. It is apparent that the reaction involves formation of the cyclohexyl radical, since ca. 1% cyclohexyl chloride was detected when the oxidation was performed in the presence of CCl_4 (entry 8). Product yields from the oxidations of relatively inert substrates were comparatively low (e.g., entries 6, 7, and 14), presumably because reduction of **2** by acetonitrile became significant (see above). Oxidation of methylcyclohexane (entry 11) and adamantane (entry 12) occurred at the tertiary C−H bond exclusively with no detectable products from sec-

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[12] Wong, K. Y.; Lee, W. O.; Che, C. M.; Anson, F. C. *J. Electroanal. Chem.* **1991**, *319*, 207.

[13] Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

[14] Lee, W. O. Ph.D. Thesis, The University of Hong Kong, 1989.

[15] 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.

[16] Cheng, W. C.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1063.

[17] Che, C. M.; Yam, V. W. W. *Adv. Inorg. Chem.* **1992**, *39*, 233.

[18] Cheng, W. C.; Yu, W. Y.; Li, C. K.; Che, C. M. *J. Org. Chem.* **1995**, *60*, 6840.

Table 2. Competitive Oxidation of Organic Substrates (1 mmol) by *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2](ClO_4)_2$ (50 mg, 0.06 mmol) in Acetonitrile (3 mL) at Room Temperature under a N_2 Atmosphere; Reaction Time 0.5 h

entry	substrates	products (yield/%)[a]	relative reactivity per H atom
1	cyclohexane and cyclopentane	cyclohexanone (20)	1
		cyclopentanone (8)	0.48
2	cyclohexane and cyclooctane	cyclohexanone (13)	1
		cyclooctanone (27)	1.6
3	cyclohexane and cyclodecane	cyclohexanone (2)	1
		cyclodecanone (14)	4.2
4	cyclohexane and cumene	cyclohexanone (4)	1
		2-phenyl-2-propanol (52)	144
		acetophenone (22)	
5	cyclohexane and adamantane	cyclohexanone (1)	1
		adamantan-1-ol (56)	84
6	cyclohexanol and cyclooctanol	cyclohexanone (9)	1
		cyclooctanone (52)	5.8

[a] Product yield is based on the amount of ruthenium complex used.

ondary C−H bond oxidation. Because the oxidation of *cis*-decalin to *cis*-decalinol is highly stereoretentive (entry 17), we suggest that the alkane oxidations proceed via a H-atom abstraction pathway with rapid radical recombination. Dimethyl sulfide was oxidized to a mixture of dimethyl sulfoxide and dimethyl sulfone (entry 21). A related report using *cis*-$[Ru^{VI}(Me_3tacn)O_2(CF_3CO_2)]^+$ as oxidant showed that dimethyl sulfide is oxidized to dimethyl sulfone only.[16]

In competitive experiments of cyclohexane/cycloalkanes in acetonitrile at 298 K using complex **2** as a stoichiometric oxidant (Table 2, entries 1−3), the relative reactivities per H atom (normalized) follow the order: cyclodecane (4.2) > cyclooctane (1.6) > cyclohexane (1) > cyclopentane (0.48). The results of analogous competitive experiments between cyclohexane/cumene, cyclohexane/adamantane, and cyclohexanol/cyclooctanol are also listed in Table 2. The employment of such competitive experiments to distinguish between radical and Gif chemistry has been proposed.[19] Hence, it is pertinent to compare the reactivities of complex **2** with the oxidation chemistry of Gif reactions. On the basis of the C_5/C_6 ratio (0.48 for **2** in CH_3CN, 0.60−0.85 for Gif in pyridine[20]) and the kinetic isotope effect for cyclohexane oxidation (6.5 for **2**, 2.1−2.3 for Gif[20]), *it is apparent that **2** and Gif systems behave differently toward alkane oxidations*. Furthermore, the relative order of reactivities for cycloalkane oxidations by complex **2** contrasts with that in Fe(III)-catalyzed Gif oxidations, whereby the relative reaction rates per hydrogen for cyclooctane is smaller than for cyclohexane.[19b] The substantial increase in the oxidation reactivity of **2** from cyclohexane to adamantane is consistent with the stability of the alkyl radicals generated through H-atom abstraction, i.e., tertiary C−H bonds are weaker than secondary.

Catalytic Oxidations by *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ (1) and TBHP. Efforts have been made to harness this class of complexes for catalytic oxidations through the use of a terminal oxidant, namely *tert*-butyl hydroperoxide (TBHP), and complex **1** was employed as the catalyst since it is relatively stable and robust. We have indeed observed catalytic alkane oxidations based on the "**1** + TBHP" system (Table 3), and *product analyses have revealed notable differences compared to stoichiometric oxidations by **2*** (preliminary results have been communicated[9c]). In control experiments, no oxidized product was detected in the absence of either the ruthenium catalyst or TBHP. Examination of the reaction medium by UV−vis spectroscopy after alkane oxidation indicated that complex **1** remains intact. Cyclohexane was oxidized to a mixture of cyclohexanol and cyclohexanone (ratio 1:1.6; entry 1), but the latter was formed exclusively in the stoichiometric oxidation. We note that other ruthenium−oxo complexes have been reported to oxidize cyclohexane to give cyclohexanone exclusively.[17] In the presence of 5-fold excess 2,6-di-*tert*-butyl-4-methylphenol (ionol), no oxidized product was detected (entry 2). When the reaction was carried out in an acetone/CCl_4 (9:1 v/v) mixture, formation of the oxygenated product(s) was suppressed and cyclohexyl chloride was afforded (entry 3). Oxidation of cyclohexane was completely inhibited if CH_3CN was used as solvent instead of acetone (entry 4); presumably acetonitrile prevents the oxidation

Table 3. Oxidation of Alkanes (1.5 mmol) with TBHP (3.2 mmol) Catalyzed by *cis*-$[Ru^{II}(6,6'\text{-}Cl_2Bpy)_2(OH_2)_2](CF_3SO_3)_2$ (0.001 mmol) in Acetone (3 mL) at Room Temperature; Reaction Time 24 h, unless Otherwise Stated

entry	substrates	product(s)	yield (%)[a]
1	cyclohexane	cyclohexanol	33
		cyclohexanone	52 ($k_H/k_D = 4.8$)
2	cyclohexane[b]	−	−
3	cyclohexane[c]	cyclohexanol	28
		cyclohexanone	41
		cyclohexyl chloride	11
4	cyclohexane[d]	−	−
5	cyclohexane[e]	cyclohexanol	13
		cyclohexanone	19
		acetophenone	49
6	cyclooctane	cyclooctanol	8
		cyclooctanone	77
7[f]	adamantane	adamantan-1-ol	62
		adamantan-2-ol and -2-one	25
8	cumene	2-phenyl-2-propanol	61
		acetophenone	29
9[g]	ethylbenzene	acetophenone	71
		sec-phenethyl alcohol	18
10[f]	*n*-hexane	*n*-hexan-2-o1	2
		n-hexan-2-one	12
		n-hexan-3-ol	3
		n-hexan-3-one	12
11	*cis*-decalin	*cis*-decalinol	15
		trans-decalinol	62

[a] Product yield is based on conversion of alkane. [b] In the presence of 5-fold excess of ionol. [c] Acetone:CCl_4 = 9:1. [d] Acetonitrile was used as solvent. [e] CHP was used as terminal oxidant. [f] Substrate = 1 mmol and TBHP = 3.2 mmol. [g] Reaction time = 48 h.

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(19) For example, see: (a) Barton, D. H. R.; Csuhai, E.; Doller, D.; Ozbalik, N.; Senglet, N. *Tetrahedron Lett.* **1990**, *31*, 3097. (b) Barton, D. H. R.; Launay, F.; Le Gloahec, V. N.; Li, T.; Smith, F. *Tetrahedron Lett.* **1997**, *38*, 8491.

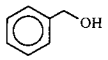
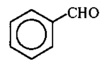
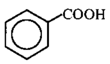
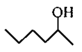
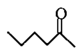
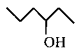
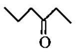
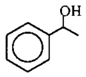
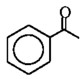
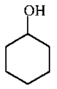
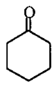
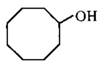
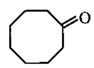
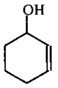
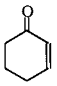
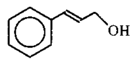
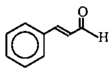
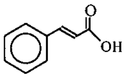
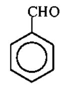
(20) Barton, D. H. R.; Doller, D.; Geletii, Y. V. *Tetrahedron Lett.* **1991**, *32*, 3811.

reaction by binding to the Ru(II) center. Cyclooctane was oxidized to yield a mixture of cyclooctanol and cyclooctanone in a ratio of 1:10 (entry 6). Oxidation of adamantane occurred preferentially at the tertiary carbon atoms to yield adamantan-1-ol (entry 7), but unlike the stoichiometric oxidation, significant amounts of products arising from secondary C−H bond oxidation were found. The smaller kinetic isotope effect ($k_H/k_D = 4.8$) and the tertiary to secondary C−H bond relative reactivities ($k_{tert}/k_{sec} = 7.4$; statistical factor corrected) in the catalytic cyclohexane and adamantane oxidations, respectively, contrast sharply with the stoichiometric oxidation results. Significantly, Drago and co-workers have reported very similar data for the catalytic $[Ru(dmp)_2(OH_2)_2](PF_6)_2 + H_2O_2$ system ($k_H/k_D = 4.0$ for cyclohexane; $k_{tert}/k_{sec} = 7.1$ for adamantane; dmp = 2,9-dimethyl-1,10-phenanthroline), for which a free-radical mechanism was proposed.[4] Furthermore, the "**1** + TBHP" protocol is capable of oxidizing linear chain alkanes such as *n*-hexane (entry 10). Thus, the active intermediate in the catalytic oxidations is unlikely to be a ruthenium−oxo derivative, or at least solely this species. Indeed, our results from the cyclohexane oxidations suggest that the active species has substantial radical character: (a) addition of ionol suppressed the catalytic oxidation (entry 2); (b) a substantial amount of cyclohexyl chloride was produced in the presence of CCl_4 (entry 3); (c) when the terminal oxidant was changed from TBHP to cumene hydroperoxide (CHP), the product profile is dominated by acetophenone, which is generated by β-scission of cumyloxy radicals (entry 5). We also note that stirring a mixture of TBHP (0.3 mL) and **1** (2 mg) in dichloromethane (3 mL) at room temperature for 20 h resulted in the formation of acetone, albeit in very low yield (<1% based on TBHP).

We investigated the competitive oxidation of cyclohexane/cyclopentane using the "**1** + TBHP" protocol and found that the relative reactivity per H atom for cyclopentane (0.38 based on cyclohexane) differed slightly from the stoichiometric oxidation by **2** (0.48). For cyclohexane/cumene, cumene was 19 times more reactive than cyclohexane; this is in contrast to the stoichiometric oxidation where cumene was 144 times more reactive. Similarly in the competitive oxidation of cyclohexanol/cyclooctanol, cyclooctanol was 1.4 times more reactive than cyclohexanol, compared to a reactivities ratio of 6 found in the stoichiometric reactions. These observations further imply that the active species in the stoichiometric and catalytic oxidations are not identical.

Our investigation showed that complex **1** is also an efficient catalyst for the oxidation of alcohols by TBHP (Table 4). Treatment of benzyl alcohol (1 mmol) with TBHP (3 mmol) in the presence of **1** in acetone (3 mL) afforded a mixture of benzaldehyde and benzoic acid in a ratio of 2:1 (87% conversion) after stirring for 24 h at ambient temperature (entry 1). When 1.2 equiv of TBHP was used, the ratio increased to 12:1 (47% conversion). Changing the solvent to CH_2Cl_2 led to decreased catalytic activity, and the reaction solution became yellow in color. Aliphatic, cyclic, and allylic alcohols were efficiently converted into the corresponding aldehydes and ketones in high to quantitative yields in the presence of excess TBHP (3−6 equiv). While oxidation of primary alcohols (entry 1) afforded a mixture of the corresponding aldehyde and acid, secondary alcohols such as 2-hexanol (entry 2) and 3-hexanol (entry 3) gave the analogous ketones. Likewise, *sec*-phenethyl alcohol (entry 4) was oxidized to acetophenone. With cyclic alcohols such as cyclohexanol (entry 5) and cyclooctanol (entry 6), the corresponding ketones were obtained without the formation of ring-opened products. With allylic alcohol like 2-cyclohexen-1-ol (entry 7), alcohol oxidation prevailed over alkene epoxidation to yield 2-cyclohexen-1-one as the sole product. In the oxidation of *trans*-cinnamyl alcohol (entry 8), the *trans*-aldehyde together with the *trans*-acid and the cleavage product benzaldehyde were observed.

Table 4. Oxidation of Alcohols (1 mmol) Catalyzed by *cis*-$[Ru^{II}(6,6'-Cl_2Bpy)_2(OH_2)_2](CF_3SO_3)_2$ (0.001 mmol) with TBHP in Acetone (3 mL) at Room Temperature

entry	substrates	product(s)	yield (%)[a]	conversion (%)	time (h)
1[b]			45	87	24
			23		
2[c]			93	90	72
3[c]			90	82	72
4[b]			95	96	48
5[b]			79	95	48
6[b]			97	97	48
7[b]			98	> 99	48
8[b]			30	98	48
			16		
			14		

[a] Product yield is based on conversion of alcohol. [b] Catalyst: substrate:TBHP = 1:1000:3000. [c] Catalyst:substrate:TBHP = 1:1000:6000.

Conclusion

We have illustrated that the robust bis(6,6′-dichloro-2,2′-bipyridine)ruthenium fragment can mediate the stoichiometric and catalytic oxidations of saturated C−H bonds, although our results suggest that the mechanistic pathways for the respective transformations are different. The *cis*-$[Ru^{VI}(6,6'-Cl_2bpy)_2O_2](ClO_4)_2$ complex (**2**) has a high $E°$ value and is in a select group of isolated metal−oxo complexes that can oxidize saturated hydrocarbons at ambient temperature; a hydrogen-atom abstraction pathway is proposed for these oxidations. Highly oxidizing metal−oxo species have been assumed as reactive intermediates in Gif oxidation chemistry, yet differences are apparent between the reactivities of the *cis*-dioxoruthenium(VI) complex **2** and Gif-type systems toward C−H bond oxidations, notably in the competitive oxidations of cycloalkanes. The "**1** + TBHP" protocol for catalytic oxidations of hydrocarbons and alcohols has been developed. Mechanistically, our results from this system are fully consistent with a free-radical process. Finally, data from these studies indicate that the oxidations of saturated hydrocarbons by complex **2**, the "**1** + TBHP" protocol and Gif-type systems are not alike from a mechanistic viewpoint.

Experimental Section

General. 6,6′-Dichloro-2,2′-bipyridine[21] and *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2Cl_2$]·$2H_2O$[12] were prepared by literature procedures. *tert*-Butyl hydroperoxide (80% in di-*tert*-butylperoxide) was purchased from Merck and the concentration was standardized by iodometric titration. All organic substrates were obtained from Aldrich and purified by literature methods, and their purity were verified by GC or ^{1}H NMR analysis before use. Solvents were of analytical grade and used as received. Silver trifluoromethanesulfonate (99+ %, Aldrich) was dried in a vacuum oven prior to use.

Preparation of *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$ (1). A mixture of *cis*-[Ru^{II}(6,6′-Cl_2bpy)$_2Cl_2$]·$2H_2O$ (0.50 g, 0.76 mmol) and Ag(CF_3SO_3) (0.59 g, 2.28 mmol) in water (40 mL) was heated at 70 °C for 30 min. The red solution was then filtered to remove AgCl. The red crystalline solid obtained by slow removal of the solvent was collected, washed with diethyl ether, and dried in vacuo. Yield = 0.47 g, 70%. Anal. Calcd for $C_{22}H_{16}N_4O_8Cl_4F_6RuS_2$: C, 29.84; H, 1.82; N, 6.33. Found: C, 29.45; H, 2.05; N, 5.95. ^{1}H NMR (CD_3CN): δ 7.60 (dd, 2H), 7.81 (dd, 2H), 8.09 (t, 2H), 8.18 (t, 2H), 8.36 (dd, 2H), 8.41 (dd, 2H). FAB-MS: m/z 587 $[M]^+$ and 551 $[M - 2(H_2O)]^+$. UV λ_{max}, nm (ϵ, dm^3 mol^{-1} cm^{-1}) in H_2O: 247 (14700), 306 (44100), 494 (9100).

Preparation of *cis*-[Ru^{VI}(6,6′-Cl_2bpy)$_2O_2$](ClO_4)$_2$ (2).[12] Complex **1** (0.10 g, 0.11 mmol) was dissolved in a minimum amount of warm water (50 °C). The resulting solution was filtered and cooled in an ice bath. Upon addition of an aqueous solution of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (2 g in 5 mL H_2O) containing $NaClO_4$ (0.5 g), the color of the solution changed from deep red to greenish-yellow immediately. A greenish-yellow solid slowly precipitated from the solution and this was collected, washed with ice-cold water, and dried in vacuo. Yield = 0.05 g, 60%. IR: 846, 860 cm^{-1} (Ru═O).

General Procedure for Stoichiometric Oxidations by Complex 2. A solution of the organic substrate (100 mg) and complex **2** (50 mg, 0.06 mmol) in degassed acetonitrile (3 mL) was stirred at room temperature under a nitrogen atmosphere for 30 min. A control experiment without the ruthenium complex was performed under identical conditions. The aliquot was analyzed on a capillary gas chromatograph equipped with a flame ionization detector. Products were quantified by the internal standard method, and identifications were achieved by comparing the retention times with authentic samples. For the oxidation of *cis*- and *trans*-stilbenes, ^{1}H NMR analysis was used for the determination of stilbene oxides.

General Procedure for Catalytic Oxidations by Complex 1 and TBHP. To a solution of organic substrate (1.5 mmol) and TBHP (3.2 mmol) in acetone (3 mL) was added complex **1** (0.001 mmol), and the mixture was stirred for 24 h at room temperature. A control experiment without the catalyst was performed under identical conditions. The aliquot was analyzed as above.

Acknowledgment. We are grateful for financial support from The University of Hong Kong and the Research Grants Council of the Hong Kong SAR, China [HKU 7092/98P]. Dr. K. K. Cheung is thanked for the structural determination of complex **1**.

Supporting Information Available: ORTEP plot and listings of crystal data, atomic coordinates, calculated coordinates, anisotropic displacement parameters, and bond lengths and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Ogawa, S.; Shiraishi, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2527.