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Chemoselective Oxidation of Alcohols to Aldehydes and Ketones by *tert*-Butyl Hydroperoxide Catalyzed by a Ruthenium Complex of *N*,*N*′,*N*″-Trimethyl-1,4,7-triazacyclononane

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An operationally simple method based on [Cn*$Ru^{III}(CF_3CO_2)_3{\cdot}H_2O$] (Cn* = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane) catalyst and 1−1.2 equiv of *tert*-butyl hydroperoxide as terminal oxidant is effective for selective transformation of alcohols to aldehydes and ketones in methylene chloride. The reaction proceeds in high yield and selectivity. Preparation of benzaldehyde (98% yield) from benzyl alcohol on a 200 mmol scale can be performed without modification of the procedure such as slow addition of the oxidant or cooling to 0 °C, and catalyst turnovers of 700 are achieved. Oxidation of geraniol which contains an isolated trisubstituted C═C bond leads to geranial selectively without oxidation of the C═C bond. Results from Hammett correlation studies ($\rho = -0.47$) and primary kinetic isotope effect ($k_H/k_D = 4.8$) for the catalytic benzyl alcohol oxidations are inconsistent with an oxoruthenium (O═Ru) based mechanism. A mechanism involving reactive tBuO$^{\bullet}$/tBuOO$^{\bullet}$ radicals is also excluded based on results from previous works: Cheng, W.-C.; Fung, W.-H.; Che, C.-M. *J. Mol. Catal. (A)* **1996**, *113*, 311; absence of di-*tert*-butyl peroxide; and using cumyl hydroperoxide as a radical probe. A *tert*-butylperoxoruthenium complex is postulated to be the active intermediate.

Introduction

Oxidation of alcohols to carbonyl compounds is an important transformation in synthetic organic chemistry. Although several stoichiometric reagents based on activated dimethyl sulfoxide (Swern oxidation),[1] hypervalent iodine compounds (Dess−Martin),[2] and reactive oxometal compounds[3] (MnO_2 and pyridinium chlorochromate) have been developed to display high degree of selectivities, the search for new catalytic procedures for selective alcohol oxidations using inexpensive oxidants such as H_2O_2[4,5] and *tert*-butyl hydroperoxide (TBHP)[6] remains an area of intensive interest. $RuCl_2(PPh_3)_3$ and some high valent oxoruthenium complexes are known to mediate alcohol oxidations using a variety of oxidants such as PhIO,[7] methylmorpholine *N*-oxide, BrO_3^-, and $S_2O_8^{2-}$ under mild conditions.[8] A notable example is tetra-*n*-propylammonium perruthenate(VII) which is an effective catalyst for oxidation of alcohols to aldehydes by methylmorpholine *N*-oxide.[9] Despite its remarkable selectivity, the reaction usually requires two to three times excess of terminal oxidant and high catalyst loading (5 mol %) with modest catalytic turnovers around 250.

Our interest in ruthenium-mediated alcohol oxidations was initiated by our recent success to achieve highly chemoselective epoxidation of unfunctionalized alkenes using the "[Cn*$Ru^{III}(CF_3CO_2)_3{\cdot}H_2O$] + tBuOOH" system (Cn* = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane).[10] The reaction exhibits good chemoselectivity toward epoxides formation with retention of configuration of the starting alkenes, i.e., *trans*-alkenes to *trans*-epoxides; *cis*-alkenes to *cis*-epoxides. Herein is described that the same system can bring about chemoselective oxidation of alcohols to aldehydes/ketones with high turnovers (Scheme 1). Our findings demonstrate the potential synthetic utilities of this protocol and suggest a *tert*-butylperoxoruthenium complex as a possible reactive intermediate.

Results and Discussion

Treatment of benzyl alcohol (1 mmol) with TBHP (1−1.2 mmol, 3.33 M in 1,2-dichloroethane) in the presence of catalytic quantity of [Cn*$Ru^{III}(CF_3CO_2)_3{\cdot}H_2O$] complex (**1**) (1 mol %) in methylene chloride (5 mL) afforded

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[1] Lee, T. V. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 291.

[2] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

[3] (a) Ley, S. V.; Madin, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 251. (b) Mijs, W. J.; DeJonge, C. R. H. I. *Organic Synthesis by Oxidation with Metal Compounds*; Plenum: New York, 1986.

[4] For some selected examples of Mo(VI) and W(VI) catalyzed alcohol oxidations, see (a) Sato, K.; Aoki, M.; Takagi, J.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 12386 and references therein. (b) Bailey, A. J.; Griffith, W. P.; Parkin, B. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1833. (c) Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2661.

[5] (a) Manganese-catalyzed benzyl alcohol oxidations, see: Zondervan, C.; Hage, R.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1997**, 419. (b) $CH_3Re^{VII}O_3$-catalyzed alcohol oxidations, see: Murray, R. W.; Iyanar, K.; Chen, J.-X.; Wearing, J. T. *Tetrahedron Lett.* **1995**, *36(36)*, 6415 (c) For [Ru]: Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 2424.

[6] Several metals have been reported to mediate TBHP oxidation of alcohols: for [Cr], see: (a) Muzart, J. *Chem. Rev.* **1992**, *92*, 113. For [Mo]: (b) Trost, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, *25(2)*, 173. (c) Masuyama, Y.; Takahashi, M.; Kurusu, Y. *Tetrahedron Lett.* **1984**, *25(39)*, 4417. For [Se]: (d) Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837. For [Ru]: (e) Tanaka, M.; Kobayashi, T.; Sakakura, T. *Angew. Chem., Intl. Ed. Engl.* **1984**, *23*, 518. (f) Murahashi, S. I.; Naota, T. *Synthesis* **1993**, 433.

[7] Müller, P.; Godoy, J. *Tetrahedron Lett.* **1981**, *22(25)*, 2361.

[8] (a) Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179. (b) Bailey, A. J.; Cother, L. D.; Griffith, W. P.; Hankin, D. M. *Transition Met. Chem.* **1995**, *20*, 590.

[9] (a) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625. (b) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.

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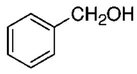
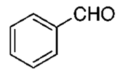
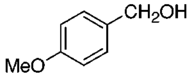
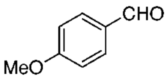
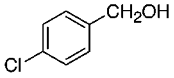
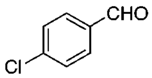
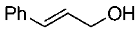
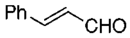
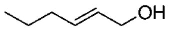
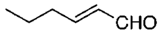
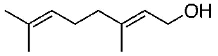
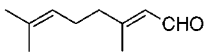
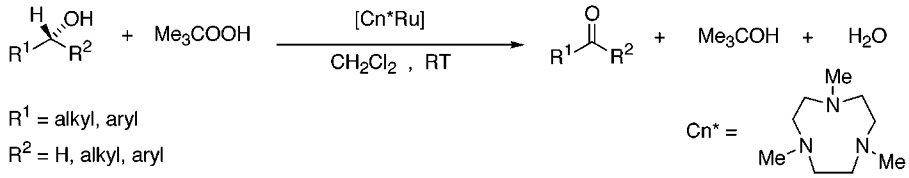
Table 1. Ruthenium-Catalyzed Oxidation of Primary Benzyl and Allyl Alcohols to Aldehydes Using TBHP

entry	alcohols	% conversion	products	yield % [a]
1		70		88 [b]
2		75		86 [b]
3		72		83 [b]
4		75		89
5		67		90
6		97		84

Reaction conditions: To a mixture of alcohols (1 mmol) and Ru catalyst (1 mol%) in methylene chloride (5 mL) was added 1 —1.2 equiv. of TBHP (3.33 M in 1,2-dichloroethane). The reaction mixture was stirred at room condition for 12 h, and aliquots were analyzed by gas chromatography. a: Yield were determined by GLC based on % conversion of alcohols. b: Small quantity of benzoic acids (<5%) were detected.

Scheme 1



benzaldehyde in 88% yield after stirring for 12 h at room temperature (Table 1). The production of di-*tert*-butyl peroxide due to decomposition of TBHP is negligible. When 2 equiv of TBHP was used, at full benzyl alcohol conversion, benzoic acid was formed as the major product (benzaldehyde-to-benzoic acid ratio = 40:60). Methylene chloride is the solvent of choice. Complex **1** in acetone showed a much reduced catalytic activity toward benzyl alcohol oxidation by TBHP, whereas the reaction was inhibited when carried out in methanol. Irrespective of this, the reaction is unretarded by atmospheric moisture and, therefore, can be conducted without the need of inert atmosphere. The ruthenium-catalyzed reaction can be conveniently scaled-up to oxidize 200 mmol of benzyl alcohol to benzaldehyde without modification of the procedure, such as slow addition of the oxidant or cooling to 0 °C. With the use of 200 mmol of TBHP and 0.1 mol % of **1** in methylene chloride, benzaldehyde was isolated in 97% yield,[11] and up to 700 catalyst turnovers were achieved.

Primary allyl alcohols (entries 4−6) were all selectively oxidized to corresponding aldehydes without oxidation of the C=C bond or overoxidation to carboxylic acids when subjecting the alcohols to the standard reaction conditions, i.e., 1 equiv of TBHP and 1 mol % Ru in CH_2Cl_2. Addition of another 1 equiv of THBP to the reaction mixtures would produce α,*β*-unsaturated acids in 95% isolated yield. As previously noted, electron deficient alkenes are poor substrates for the "[Cn*Ru] + *t*BuOOH" system;[10] therefore, no effective epoxidation of the C=C bond of the α,*β*-unsaturated acids was observed upon addition of further quantity of TBHP. It is worthy to mention that geraniol (entry 6), which contains an isolated trisubstituted C=C bond, can be oxidized to geranial in 84% yield; yet no epoxidation products were detected if only 1 equiv of TBHP was used. Oxidation of primary aliphatic alcohols such as *n*-octanol is ineffective by this Ru-catalyzed reaction, and the starting alcohols are recovered.

Likewise secondary alcohols are converted to ketones (Table 2) when treated with 1.2 equiv of TBHP in the presence of 1 mol % Ru catalyst at slightly elevated temperature (40 °C). Under such conditions, 1-phenylethanol and benzhydrol were efficiently oxidized to acetophenone (entry 1) and benzophenone (entry 2), respectively, as well as some aliphatic secondary alcohols to their ketones (entries 4−8). Oxidation of cyclohexenol afforded cyclohexenone selectively (entry 3); again addition of further quantity of TBHP did not lead to C=C oxidation. Cyclic aliphatic alcohols (C_4, C_6, and C_8) were

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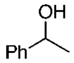
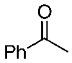
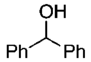
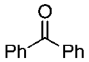
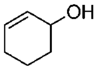
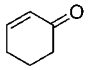
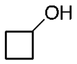
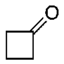
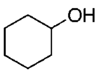
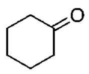
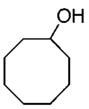
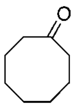
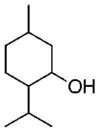
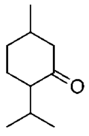
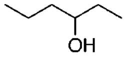
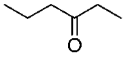
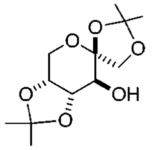
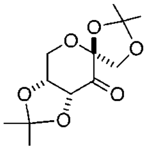
[11] Benzyl alcohol was consumed by 70%, and benzaldehyde was isolated in 97% yield based on the amount of alcohol consumed.

Table 2. Ruthenium-Catalyzed Oxidation of Secondary Alcohols to Ketones Using TBHP

entry	alcohols	% conversion	products	yield % [a]
1		82		93
2		83		92
3		100		89
4		64		89
5		62		87
6		71		90
7		59		92
8		47		93
9		61		95

Reaction conditions: To a mixture of alcohols (1 mmol) and Ru catalyst (1 mol%) in methylene chloride (5 mL) was added 1 —1.2 equiv. of TBHP (3.33 M in 1,2-dichloroethane). The reaction mixture was stirred at 40°C for 12 h, and aliquots were analyzed by gas chromatography. a: Yield were determined by GLC based on % conversion of alcohols.

Table 3. Listing of k_{rel} and σ Values for the Ru-Catalyzed Oxidation of *Para*-Substituted Benzyl Alcohols

entry	Y	k_{rel}	σ
1	MeO	1.38	−0.28
2	Me	1.24	−0.14
3	H	1.00	0.00
4	F	0.93	+0.15
5	Cl	0.78	+0.24
6	CF_3	0.58	+0.53

all selectively oxidized to the corresponding ketones without formation of the ring opening products (entries 4−6), in contrast to the oxidation of cyclobutanol by $Ru^{VII}O_4^-$ in which case 1-butanal is produced.[12]

The effect of *para*-substituents on the catalytic benzyl alcohol oxidations has been investigated. The relative rates for the catalytic oxidation of several *para*-substituted benzyl alcohols (p-Y−$C_6H_4CH_2OH$, Y = MeO, Me, H, F, Cl, and CF_3), k_{rel}, were evaluated by monitoring the reactions with gas chromatography (see Experimental Section). Figure 1 depicts a linear correlation ($R = 0.994$) of log k_{rel} [$k_{\mathrm{rel}} = k(p\text{-Y}-C_6H_4CH_2OH)/k(C_6H_5CH_2OH)$] vs substituent constants σ. The slope of the plot ($\rho = -0.47$) is much smaller than those ($\rho = -1.2$ to -1.9)[13] observed in the stoichiometric benzyl alcohol oxidations by the cationic dioxoruthenium(VI), $[(N_4)Ru^{VI}O_2]^{2+}$, complexes (N_4 = tertiary tetraamine macrocycles). This reveals that the electronic substituent effect exhibited by the "[Cn*Ru] + *t*BuOOH" system is considerably less pronounced. On the other hand, the correlation between the log k_{rel} values with substituent constants σ^+ is less satisfactory ($R = -0.94$). This finding together with the small negative ρ value argue against the involvement of carbocation intermediates. The primary kinetic isotope effect (k_H/k_D) for the Ru-catalyzed oxidation of benzyl alcohol and benzyl alcohol-d_7 has been found to be 4.8 (see Experimental Section). Although this value indicates substantial C−H bond cleavage on progressing to the transition

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(12) Lee, D. G.; Congson, L. N. *Can. J. Chem.* **1990**, *68*, 1774.

(13) (a) Che, C.-M.; Tang, W.-T.; Lee, W.-O.; Wong, K.-Y.; Lau, T.-C. *J. Chem. Soc., Dalton Trans.* **1992**, 1551. (b) Cheng, W.-C.; Yu, W.-Y.; Li, C.-K.; Che, C.-M. *J. Org. Chem.* **1995**, *60*, 6840.

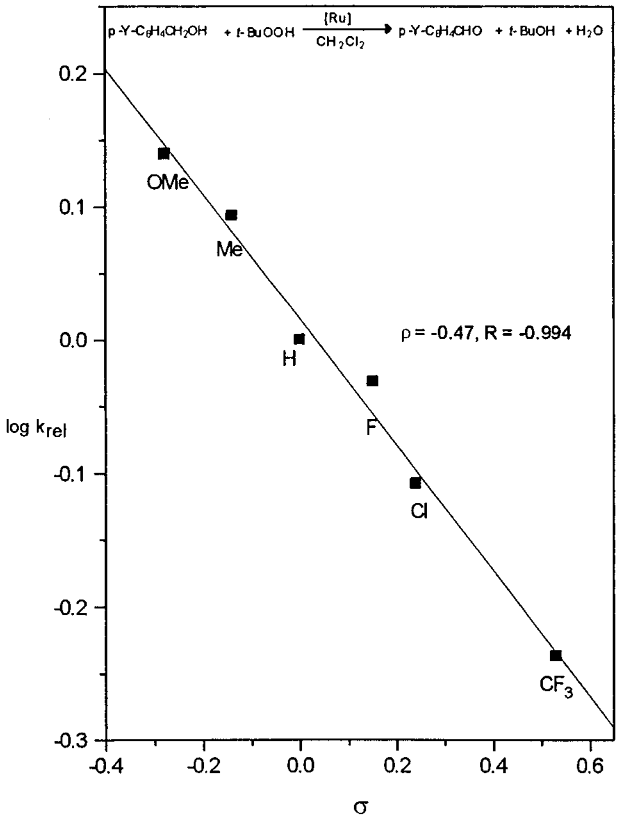


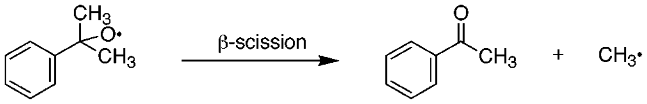
Figure 1. Hammett correlation studies (log k_{rel} vs σ) for the ruthenium-catalyzed oxidation of *para*-substituted benzyl alcohols by TBHP.

state, it is still far smaller than those found for the stoichiometric benzyl alcohol oxidations by the cationic *cis*-$[Cn^*Ru^{VI}O_2(CF_3CO_2)]^+$ (k_H/k_D = 17),[14] $[(N_4)Ru^{VI}O_2]^{2+}$ (k_H/k_D = 15−21),[13] and $[(bpy)_2(py)Ru^{IV}O]^{2+}$ (py = pyridine) complexes (k_H/k_D = 50).[15]

The action of H_2O_2 on some $[(N_4)Ru^{III}(H_2O)_2]^{3+}$ complexes has afforded the dioxoruthenium(VI), $[(N_4)Ru^{VI}O_2]^{2+}$, complexes[16] some of which have been characterized by X-ray crystallography.[16c] Their $O{=}Ru^{IV}/Ru^{V}$ derivatives can undertake electrocatalytic oxidation of benzyl alcohols.[17] *cis*-$[Cn^*Ru^{VI}O_2(CF_3CO_2)]^+$ complex was hitherto prepared by Ce(IV) oxidation of **1** in 0.1 M CF_3CO_2H, and its structure was established by X-ray crystallography.[18] However, the UV/vis spectra of **1** in the presence of excess H_2O_2 or TBHP lack any distinctive features in 300−700 nm range, as opposed to *cis*-$[Cn^*Ru^{VI}O_2(CF_3CO_2)]^+$ complex which shows intense absorption at ca. 340 nm (ϵ = 2400) and a weak absorption at ca. 695 nm (ϵ = 50) in 1 M CF_3CO_2H. Apparently, the dioxoruthenium(VI) complex is not generated on treatment with excess peroxides under ambient condition. Furthermore, results from Hammett correlation studies (small ρ value) and primary kinetic isotope effect (small k_H/k_D) for the catalytic benzyl alcohol oxidations do not warrant an oxoruthenium (O=Ru) based mechanism.

The observed small k_H/k_D value could be a manifestation of a free radical chain mechanism where *t*BuO• and/or *t*BuOO• species are the active agents. Yet the reactive intermediate generated from the "[Cn*Ru] + *t*BuOOH" system can effect stereoselective epoxidation of unfunctionalized alkenes (*cis*-alkenes → *cis*-epoxides),[10] which is characteristic of an "oxene" (two-electron oxidant) species.[19] The absence of di-*tert*-butyl peroxide, formed by the homocoupling of *t*BuO• radicals, has also discounted the possibility of a free radical chain mechanism. This notion is further scrutinized by employing cumyl hydroperoxide as a mechanistic probe, because once the hydroperoxide yields cumyloxy radicals, it will undergo facile β-scission to form acetophenone and a methyl radical (Scheme 2).[20] Under typical reaction conditions, alcohol (1 mmol), cumyl hydroperoxide (1 mmol), and **1** (1 mol %) in methylene chloride, benzyl alcohol was effectively converted to benzaldehyde in 91% yield at 74% substrate conversion without the formation of acetophenone. This strongly supports that the "[Cn*Ru] + *t*BuOOH" system should not operate via reactive alkoxy radicals resulting from ruthenium-catalyzed TBHP decomposition analogous to Fenton-type chemistry.

Scheme 2



The mechanistic findings have led us to propose a reactive *tert*-butylperoxoruthenium species, Ru−OO*t*-Bu,[21] as the active intermediate for the ruthenium-catalyzed TBHP oxidation of alcohols, although no definitive structural assignment (e.g. monomeric vs bridging dimer) can be made. Reports on peroxo complexes for early transition metals are numerous,[22] and the synthetic values of some peroxo complexes of Ti(IV), V(V), and Mo(VI) have been well documented in the literature.[23] On the contrary, reactive peroxoruthenium complexes are relatively sparse, and studies on their synthetic utilities in organic oxidations[24] are largely in its infancy. None-

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theless some peroxoruthenium complex supported on phosphine ligands have been characterized by X-ray crystal analysis.[25]

Conclusion

[$Cn^*Ru^{III}(CF_3CO_2)_3 \cdot H_2O$] complex is proven to be an active catalyst for selective oxidation of alcohols to aldehydes and ketones using inexpensive TBHP under mild conditions. The present methodology is operationally simple and has avoided the use of large excess of oxidant. Regardless of the mechanistic details, we anticipate that this catalytic system would be potentially useful for practical organic synthesis.

Experimental Section

Materials. The alcohols employed in this study were obtained from commercial sources and purified either by distillation or crystallization, and the purity of each was verified by GLC before use. Solvents were of analytical grade and used as received. *tert*-Butyl hydroperoxide, purchased from Aldrich as 70% aqueous solution, was pretreated by following the procedures described by Sharpless and coworkers using 1,2-dichloroethane and was later standardized by iodometric titration (3.33 M in 1,2-dichloroethane).[26] Silver trifluoromethanesulfonate (99+%, Aldrich) was dried in a vacuum oven prior to use. Trifluoroacetic acid (99%, Aldrich) was purified by distillation under inert atmosphere. Deionized water was distilled over alkaline $KMnO_4$ before use. [$Cn^*Ru^{III}Cl_3$] was prepared by the literature procedure.[27]

Procedure for the Preparation of [$Cn^*Ru^{III}(CF_3CO_2)_3 \cdot H_2O$] Complex (1).[10] A mixture of [$Cn^*Ru^{III}Cl_3$] (0.2 g, 0.53 mmol) and CF_3SO_3Ag (0.45 g, 1.75 mmol) in aqueous trifluoroacetic acid (0.2 M, 30 mL) was refluxed for 1 h. The solution was hot filtered to remove the insoluble AgCl. The pale-red filtrate was then heated at 70 °C until the volume of the solution was reduced to ca. 10 mL. Deposition of pale-yellow microcrystalline solids would occur gradually on cooling. The solid was then collected on a frit, washed with ice-cold deionized water, and dried in vacuo (yield = 0.25 g, 70%). Positive-ion FAB-MS: $m/z = 499$ [$M - H_2O - CF_3CO_2$]. Anal. Calcd for $C_{15}H_{23}F_9N_3O_7Ru$: C, 28.62; H, 3.68; N, 6.68. Found: C, 27.67; H, 3.58; N, 6.35. **1** is tentatively formulated as [$Cn^*Ru^{III}(CF_3CO_2)_3 \cdot H_2O$] based on elemental analysis and FAB-MS.[28]

Procedure for the Ruthenium-Catalyzed Alcohol Oxidations by TBHP. To a mixture of alcohol (1 mmol) and **1** (1 mol %) in methylene chloride (5 mL) was added TBHP (1−2 mmol, 3.33 M in 1,2-dichloroethane). The homogeneous solution was stirred at room temperature for 12 h. Aliquots were then analyzed by GLC equipped with a Supelco SPB-5 capillary column. Components were identified by comparing their retention times with those of authentic samples. Internal standard method was employed to quantify the products as well as alcohols consumption. The product yields were based on the amount of alcohols consumed in the reactions.

Procedure for the Catalytic Benzyl Alcohol Oxidation by TBHP (200 mmol scale). To a mixture of benzyl alcohol (200 mmol) and **1** (0.1 mol %) in methylene chloride (100 mL) was added TBHP (200 mmol, 3.33 M in 1,2-dichloroethane), and the solution was stirred at room temperature for 20 h. Solvent was removed by rotary evaporation, and diethyl ether (50 mL) was added to precipitate the catalyst. The ethereal solution was filtered through Celite and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using hexane:diethyl ether (9:1) as the eluant. Benzaldehyde was isolated in 97% yield (based on 70% alcohol conversion).

Determination of the Relative Reactivities (k_{rel}) for the Catalytic Oxidation of *Para*-Substituted Benzyl Alcohols. A solution containing benzyl alcohol (1 mmol), substituted benzyl alcohol (1 mmol), 1,4-dichlorobenzene (1 mmol as the internal standard), and TBHP (0.5 mmol, 3.33 M in 1,2-DCE) was prepared. The Ru catalyst **1** (0.02 mmol) was added, and the solution was stirred for 8 h. The amounts of alcohols before and after the reactions were determined by GLC. The relative reactivities were determined by eq 1.

$$k_{rel} = k_Y/k_H = \log(Y_f/Y_i)/\log(H_f/H_i) \qquad (1)$$

where Y_f and Y_i are the final and initial quantities of the substituted alcohols; *H_f and H_i are the final and initial quantities of benzyl alcohol.*

Determination of Primary Kinetic Isotope Effect (k_H/k_D) for the Catalytic Oxidation of Benzyl Alcohol and Benzyl Alcohol-d_7. A solution containing benzyl alcohol (1 mmol), *p*-chlorobenzyl alcohol (1 mmol), 1,4-dichlorobenzene (1 mmol, as the internal standard), and TBHP (0.5 mmol, 3.33 M in 1,2-DCE) was prepared. Another solution, using benzyl alcohol-d_7 instead of benzyl alcohol, was also prepared. The Ru catalyst **1** (0.02 mmol each) was added to both solutions, and the mixtures were stirred for 8 h at room temperature. The amounts of alcohols before and after the reactions were determined by GLC analysis. The k_H/k_D value was determined by using the following equations.

$$k_H/k_{Cl} = \log(H_f/H_i)/\log(Cl_f/Cl_i) \qquad (2)$$

$$k_D/k_{Cl} = \log(D_f/D_i)/\log(Cl_f/Cl_i) \qquad (3)$$

then, k_H/k_D = (eq 2)/(eq 3).

H_f and H_i are final and initial quantities of benzyl alcohol; D_f and D_i are final and initial quantities of benzyl alcohol-d_7; Cl_f and Cl_i are final and initial quantities of *p*-chlorobenzyl alcohol.

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