JOC Article

A Silica Gel-Supported Ruthenium Complex of 1,4,7-Trimethyl-1,4,7-triazacyclononane as Recyclable Catalyst for Chemoselective Oxidation of Alcohols and Alkenes by *tert*-Butyl Hydroperoxide

Wai-Hung Cheung, Wing-Yiu Yu,* Wing-Ping Yip, Nian-Yong Zhu, and Chi-Ming Che*

Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong

cmche@hku.hk

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A silica gel-immobilized [(Me_3tacn)Ru^{III}(CF_3COO)$_2$(H_2O)]CF_3CO_2 complex (**1**−SiO_2, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) was prepared by simple impregnation, and the catalyst was characterized by powdered X-ray diffraction, nitrogen adsorption/desorption, Raman, and diffuse reflectance UV−vis spectroscopies. The supported Ru catalyst can effect facile oxidation of alcohols by *tert*-butyl hydroperoxide (TBHP). Primary and secondary benzyl, allylic, and propargylic alcohols were transformed to their corresponding aldehydes and ketones in excellent yields; no oxidation of the C═C and C≡C bonds was observed for the allylic and propargylic alcohol oxidations. Likewise alkene epoxidation by TBHP can be achieved by **1**−SiO_2; cycloalkenes such as norbornene and cyclooctene were oxidized to their *exo*-epoxides exclusively in excellent yields (>95%). The **1**−SiO_2 catalyst can be recycled and reused for consecutive alcohol and alkene oxidations without significant loss of catalytic activity and selectivity; over 9000 turnovers have been attained for the oxidation of 1-phenyl-1-propanol to 1-phenyl-1-propanone. 4-Substituted phenols were oxidized by the "**1** + TBHP" protocol to give exclusively ruthenium−catecholate complexes, which were characterized by UV−vis and ESI-MS spectroscopies. No (*tert*-butyldioxy)cyclohexadienone and other radical coupling/overoxidation products were produced using the "**1** + TBHP" protocol. The formation of ruthenium−catecholate is proposed to proceed via *ortho*-hydroxylation of phenol.

Introduction

Chemoselective alcohol and alkene oxidations have a paramount importance in organic synthesis because their reaction products (i.e., aldehydes/ketones and epoxides) are key building blocks for construction of complex organic molecules.[1,2] Common laboratory-scale alcohol and alkene oxidations usually employ a stoichiometric amount of toxic and reactive oxidants such as chromium(VI) oxide, hypervalent iodine reagents (Dess−Martin),[3] and peracids[2b] that pose severe safety and environmental hazards in large-scale industrial reactions. In view of the growing environmental concerns, development of environmental-friendly and operationally safe catalytic systems for organic oxidations using more tractable reagents such as molecular oxygen, aqueous hydrogen peroxide, and *tert*-butyl hydroperoxide (TBHP) is highly desirable.[4] Advances have been made by employing Mo/W(VI),[5] Re(VII),[6] Mn(II),[7] Fe(II),[8] or Ru[9a−f] complexes as homogeneous catalysts for organic oxidations using dilute H_2O_2/TBHP as terminal oxidant. Recently promising results have been obtained with Ru,[9g−m] Pd(II),[10] and Cu(I)[11]

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* To whom correspondence should be addressed.

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complexes as homogeneous catalysts for aerobic alcohol oxidations.

Ruthenium complexes are versatile catalysts for organic synthesis.[12−15] Developing recyclable heterogeneous ruthenium catalysts for organic oxidations would be an attractive strategy to achieve easy product separation and catalyst recycling. However, few heterogeneous Ru catalysts for organic oxidations are known in the literature; notable examples include Ru-grafted hydroxyapatites[16a] and hydrotalcites[16b,c] for aerobic alcohol oxidations and supported perruthenate(VII)[16d] catalysts based on cross-linked polymer and mesoporous molecular sieves (MCM-41) for alcohol oxidations using morpholine *N*-oxide as oxidant.[16e] These reported heterogeneous catalysts, however, exhibit modest product turnover values (<1000). Previously we prepared a heterogeneous ruthenium porphyrin catalyst supported on MCM-41. This Ru−MCM-41 catalyst can effect highly efficient alkene epoxidations by 2,6-dichloropyridine *N*-oxide with up to 11000 turnovers being attained;[16g,h] however, leaching/deactivation upon successive uses of the catalyst leading to gradual decline in catalytic activity and product selectivity remains a major drawback.

Oxidation chemistry of aqua-ruthenium complexes containing macrocyclic tertiary amine ligands has been extensively investigated,[17] and their high-valent oxoruthenium derivatives are powerful oxidants.[18,19] Previously we described that $[(Me_3tacn)Ru^{III}(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (**1**) could be oxidized to a reactive *cis*-dioxoruthenium(VI) complex, *cis*-$[(Me_3tacn)Ru^{VI}O_2(CF_3CO_2)]ClO_4$, which had been structurally characterized by X-ray crystal analysis.[18b] Our earlier studies revealed that **1** is an effective and robust catalyst for homogeneous alcohol and alkene oxidations using TBHP as terminal oxidant, and more than 6000 product turnovers were attained.[9c] Compared to dilute H_2O_2, TBHP is less expensive and safer to handle in large quantities; its reaction byproduct, *tert*-butyl alcohol, is environmentally benign and easily removed.[20] In view of the robustness of **1** in homogeneous oxidation catalysis, we anticipate that an effective heterogeneous Ru catalyst could be developed by grafting **1** onto inert solid support.

As our ongoing effort to develop oxidative robust heterogeneous Ru catalysts based on molecularly defined ruthenium complexes, we set forth to prepare a new ruthenium−silica catalyst (**1**−SiO_2) by simple impregnation of **1** onto commercial chromatographic silica gel. Because of its high surface area (5−800 $m^2\ g^{-1}$) and high porosity, silica gel is a common sorbent for chromatographic separation of organic compounds. Besides, silica gel has found increasing applications in organic synthesis;[21] examples include cyclization of ketene acetals to form polyfunctional bicyclo[2.2.2]octanones[22] and Kno-

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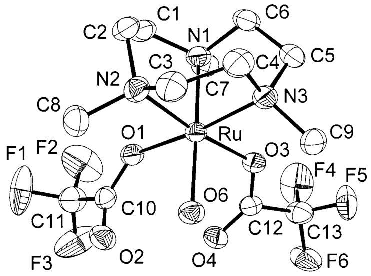

FIGURE 1. A perspective view of $[(Me_3tacn)Ru^{III}(CF_3CO_2)_2(H_2O)]^+$ cation. Bond distances (Å): Ru−O(1) = 2.078(2), Ru−O(3) = 2.028(2), Ru−O(6) = 2.111(2), Ru−N(1) = 2.080(3), Ru−N(2) = 2.090(3), Ru−N(3) = 2.086(3). Bond angles (deg): O(1)−Ru−O(3) = 92.54(9), O(1)−Ru−O(6) = 91.48(9), O(3)−Ru−O(6) = 90.89(8), O(1)−Ru−N(1) = 89.4(1), O(1)−Ru−N(2) = 92.9(1), O(1)−Ru−N(3) = 173.3(9).

evenagel condensation.[23] In this work, $\mathbf{1}-SiO_2$ is an effective catalyst for heterogeneous alcohol and alkene oxidations by TBHP, and the catalyst is readily recycled for successive reactions without showing significant deterioration of chemoselectivity and catalytic activity. Up to 9000 product turnovers have been achieved for the $\mathbf{1}-SiO_2$-catalyzed oxidation of 1-phenyl-1-propanol to 1-phenyl-1-propanone under mild conditions.

Results and Discussion

Preparation and Characterization of $[(Me_3tacn)Ru^{III}(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (1). Following our reported procedure,[9c] $[(Me_3tacn)Ru^{III}Cl_3]$ was gently refluxed with silver trifluoromethanesulfonate in 0.2 M trifluoroacetic acid. After removal of the insoluble AgCl, slow evaporation of the pale red solution by heating at or below 70 °C gave **1** as a pale yellow microcrystalline solid (see Experimental Section for details). Attempt to speed up the evaporation process by heating at above 70 °C led to a white powder, instead of a yellow crystalline solid. We found that this white powder sample gave poor catalytic activity and product selectivity for epoxidation of styrene by TBHP. As a result, only the yellow microcrystalline solid of **1** was employed for preparation of supported catalyst.

The infrared spectrum of the yellow crystalline Ru complex displays a $\nu_{C=O}$ stretch at 1713 cm^{-1}; its FAB mass spectrum exhibits two prominent ion cluster peaks at m/z = 499 and 385 assignable to $[(Me_3tacn)Ru(CF_3COO)_2]^+$ and $[(Me_3tacn)Ru(CF_3COO)]^+$ ions, respectively.

Complex **1** is insoluble in *n*-hexane, diethyl ether, CH_2Cl_2, $CHCl_3$, and CH_3CN but slowly dissolves in methanol or ethanol to give a pale yellow solution. A methanolic solution of **1** shows an intense absorption band at λ_{max} = 392 nm (ϵ_{max} = 2290 $dm^3mol^{-1}cm^{-1}$); its ESI-MS spectrum is featured by a prominent ion species at m/z = 417 that matches with the $[(Me_3tacn)Ru(CF_3COO)(OMe)]^+$ formulation. The 392 nm absorption is assigned to ligand-to-metal charge-transfer transition in nature.

The molecular structure of **1** has been determined by X-ray crystallography (see Supporting Information for details). As shown in Figure 1, the ruthenium atom adopts a distorted octahedral geometry with a coordinated H_2O molecule. The measured Ru−O(6) distance is 2.111(2) Å, which is comparable to the reported values found in $[(Me_3tacn)Ru^{II}(bpy)(H_2O)]^+$ [bpy = 2,2'-bipyridine, 2.169(3) Å],[24] $[Ru^{III}(H_2O)_6]^{3+}$ [2.016(4) − 2.037(5) Å],[25] and $[Ru^{II}(terpy)(tmea)(H_2O)]^{2+}$ [2.151(7) Å; terpy = terpyridine, tmea = *N,N,N',N'*-tetramethyl-1,2-ethanediamine].[26]

Two η^1-bound trifluoroacetate ligands coordinate to the ruthenium atom in a cis configuration. The respective Ru−O(1) and Ru−O(3) distances are 2.078(2) and 2.028(2) Å, which are comparable to the corresponding values observed in $[(Me_3tacn)(CF_3CO_2)\overline{Ru^{IV}OC_2(SiMe_3)_2O}]^+$ [2.075(6) Å] complex.[18f] The Me_3tacn ligand coordinates facially to the Ru atom with the respective Ru−N(1), Ru−N(2) and Ru−N(3) distances being 2.080(3), 2.090(3), and 2.086(3) Å, which are close to the corresponding values for $[(Me_3tacn)Ru^{II}(bpy)(OH_2)]^{2+}$ complexes [2.154(4), 2.087(4), and 2.149(5) Å].[24]

Preparation of the Silica Gel-Supported Ruthenium Catalyst. Immobilization of ruthenium catalyst was undertaken by stirring an ethanolic solution of **1** with chromatographic grade commercial silica gel at room temperature. Removal of the solvent by rotary evaporation at 40 °C afforded the heterogeneous Ru catalyst, designated as $\mathbf{1}-SiO_2$ (1%w/w), as a pale yellow solid. The FT-Raman analysis of $\mathbf{1}-SiO_2$ showed the ν_{Si-O} stretches at 795 and 877 cm^{-1} and ν_{CH} stretches at 2900 and 2979 cm^{-1} (characteristic absorption of the Me_3tacn ligand). To evaluate the Ru content, the supported catalyst was treated with concentrated HCl, followed by inductively coupled plasma (ICP) analysis. The Ru content was determined to be 0.94% w/w, which is close to the expected value of 1%w/w (see Experimental Section for detail). Both the X-ray powder diffraction (XRD) patterns of $\mathbf{1}-SiO_2$ and silica gel show a broad and featureless absorption peak at ca. 2θ = 24°, suggesting that complex **1** should be uniformly dispersed over the silica gel. The surface area of unloaded silica gel was determined to be 514.46 m^2 g^{-1} by nitrogen adsorption isotherm (BET) measurement, whereas the overall surface area of $\mathbf{1}-SiO_2$ was reduced to 483.88 m^2 g^{-1} consistent with surface immobilization of the Ru complex.

The solid diffuse-reflectance UV−vis spectrum of $\mathbf{1}-SiO_2$ shows an intense absorption band at λ_{max} = 320 nm, which is absent in unloaded silica gel sample (see Supporting Information). This absorption band is significantly blue-shifted from the absorption band of $[(Me_3tacn)Ru(CF_3COO)(OMe)]^+$. Our previous work showed that $[(Tet\text{-}Me_6)Ru^{III}(OSiMe_3)_2]^+$ (Tet-Me_6 = *N,N,N',N'*-3,6-diazaoctane-3,6-dimethyl-1,8-diamine) displays an intense ligand-to-metal charge transfer (LMCT) absorption band at λ_{max} = 340 nm.[27] We tentatively assign the 320 nm absorption band of $\mathbf{1}-SiO_2$ to a similar LMCT transition. The importance of polar Si−OH groups for immobilization of **1** is reflected by the following observa-

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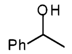
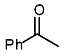
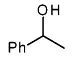
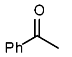
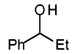
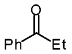
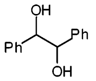
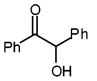
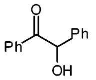
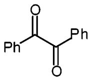
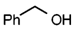
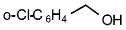
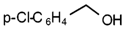
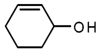
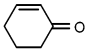
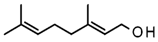
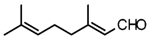
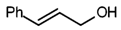
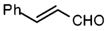
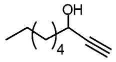
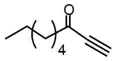
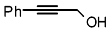
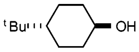
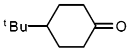
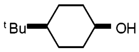
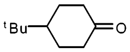
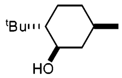
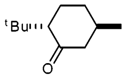
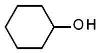
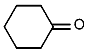
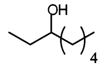
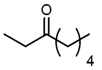
TABLE 1. Heterogeneous 1−SiO$_2$-Catalyzed Alcohol Oxidation by *tert*-Butyl Hydroperoxide

entry	substrate	time/h	%conversion	product	%yield[a]
1		16	99		94
2		16[b]	81[b]		93[b]
3		16	93		99
4		16	95		89
5		72	67		99
6		14	81	PhCHO	86
7		16	81	o-Cl-C$_6$H$_4$CHO	77
8		16	93	p-Cl-C$_6$H$_4$CHO	76
9		12	81		70
10		16	85		87
11		16	74		89
12		16	77		91
13		16	51	Ph—≡—CHO	90
14		16	90		99
15		12	96		99
16		12	11		79
17		16	41		86
18		16	50		83

Reaction conditions: A mixture of alcohol (1 mmol), **1**−SiO$_2$ (600 mg) and TBHP (2.3 mmol) in *n*-hexane (5 mL) was stirred in a screw-capped vessel at 45 °C for 12−16 h. After centrifugation, aliquots were taken from the reaction mixture for capillary GC analysis. [a] Yields were determined by capillary GC analysis based on % alcohol conversion. [b] In CH$_2$Cl$_2$.

tion: when **1**−SiO$_2$ (0.1 g) was washed with ethanol (3 × 30 mL), no leaching of the ruthenium complex was observed. However, when the silica surface was modified with hydrophobic triphenylsilyl groups, the resultant silica was ineffective for complex immobilization, and **1** can be easily washed off with ethanol. As noted in previous section, to release the Ru complex from silica support would require treatment of **1**−SiO$_2$ with concentrated HCl. We propose that grafting of **1** onto silica may involve reaction of [(Me$_3$tacn)Ru^{III}(CF$_3$CO$_2$)(H$_2$O)]$^+$ with the surface Si−OH groups to form Ru−OSi linkages.

Heterogeneous Catalytic Alcohol Oxidations. Oxidation of Benzylic Alcohols. In the presence of **1**−SiO$_2$ (1%w/w, 600 mg), 1-phenylethanol (1 mmol) was oxidized by TBHP (2.3 mmol) in *n*-hexane (5 mL) to afford acetophenone in 94% yield (99% conversion; Table 1, entry 1). Previously, CH$_2$Cl$_2$ was found to be the best solvent for the homogeneous **1**-catalyzed alcohol oxidations (80% conversion and 93% yield). However, using CH$_2$Cl$_2$ as solvent for the heterogeneous 1-phenylethanol oxidation resulted in slightly reduced substrate conversion (81%) and lower product yield (93%), when compared to the results obtained with *n*-hexane as solvent.

Likewise, 1-phenyl-1-propanol was converted to its ketone product in 99% yield (93% conversion) under the **1**−SiO$_2$ catalyzed conditions (entry 3). For oxidation of hydrobenzoin, the reaction required 16 h to achieve 95% conversion and benzoin was formed in 89% yield (entry 4), albeit with minor formation of benzil (7%). We found that further oxidation of benzoin to benzil (entry 5, 67% conversion and 99% yield) required a longer reaction time (72 h) and 3 equiv of TBHP. It is known that the tungsten-catalyzed oxidation of 1,2-diols using H$_2$O$_2$ produced aldehydes/acids as side-products.[28] In this work, no benzaldehyde formation was observed for the **1**−SiO$_2$ catalyzed hydrobenzoin/benzoin oxidation.

Benzyl alcohol and its substituted derivatives (entry 6−8) are oxidized effectively to their corresponding benzaldehydes by the "**1**−SiO$_2$ + TBHP" protocol. Unlike the 1-phenyl-1-propanol oxidation discussed in earlier section, 1.2 equiv of TBHP was required to achieve 81% conversion with 86% yield of benzaldehyde in the benzyl alcohol oxidation. When 2.3 equiv of TBHP was employed, a significant amount of benzoic acid (25%) was formed and benzaldehyde was obtained in only 57% yield. It should be noted that silica gel alone (i.e., without the immobilized Ru-catalyst) is ineffective toward oxidation of alcohols by TBHP; all the starting alcohol was fully recovered.

Oxidation of Allylic and Propargylic Alcohols. Allylic alcohols such as 2-cyclohexenol, geraniol, and cinnamyl alcohol (entries 9, 10, and 11) were selectively oxidized to the corresponding ketones/aldehydes using **1**−SiO$_2$ (600 mg) and TBHP (2.3 equiv) in *n*-hexane; no oxidation of C=C bond was observed. For the geraniol and cinnamyl alcohol oxidations, geranial and cinnamyl aldehyde were formed in 87−89% yields (entries 10−11) without overoxidation to carboxylic acids. Furthermore, no isomerization of the allylic C=C bonds was observed. We previously showed that the "**1** + TBHP" protocol can effectively epoxidize unfunctionalized alkenes under homogeneous conditions.[9d] Yet, in this work, we did not encounter any epoxidation of the isolated trisubstituted C=C bond for the **1**−SiO$_2$-catalyzed geraniol oxidation (entry 10), and no 6,7-epoxy allylic alcohols/aldehydes

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[28] Krohn. K.; Vinke, I.; Adam, H. *J. Org. Chem.* **1996**, *61*, 1467.

were detected based on ^{1}H NMR analysis of the crude product mixture.

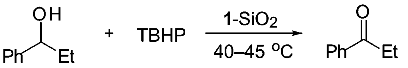
In contrast to the Swern oxidation that is ineffective for oxidation of propargylic alcohols,[29] the "**1**$-$SiO$_2$ + TBHP" protocol can also oxidize 1-octyn-3-ol and 1-phenyl-1-propyn-3-ol to their corresponding carbonyl products in ca. 90% yields (entries 12 and 13). As reported earlier, *cis*-[(Me$_3$tacn)Ru^{VI}O$_2$(CF$_3$CO$_2$)]$^+$ complex readily reacts with internal alkynes to give 1,2-diketones.[20b] However, in this work, formation of 1,2-diketones was not observed in the catalytic alkynol oxidations.

Oxidation of Aliphatic Secondary Alcohols. With **1**$-$SiO$_2$ (600 mg) and TBHP (2.3 mmol) in *n*-hexanes, aliphatic cyclic alcohols (entries 14$-$18) were converted to their ketones in ca. 80% yields. The **1**$-$SiO$_2$ catalyzed oxidation of substituted cyclohexanols can be significantly influenced by bulky substituents. For example, oxidation of 4-*cis*/*trans*-*tert*-butylcyclohexanol (entries 14 and 15) can proceed to >70% conversion in 12 h, affording the corresponding ketone product in 99% yield. Yet, the analogous reaction with menthol (entry 16) achieved only 11% conversion under the same reaction conditions. In contrast, the homogeneous **1**-catalyzed menthol oxidation was reported to attain 59% substrate conversion with 92% yield of menthone under the same reaction conditions.[9c] Assuming that the active Ru species is bound to silica surface, such reactivity difference of the heterogeneous system versus the homogeneous one is attributed to increased steric interaction of menthol with the silica gel surface (see also *trans*-stilbene oxidation in later sections).

Analogous to the homogeneous reactions,[9c] oxidation of primary alcohols such as 1-octanol by the "**1**$-$SiO$_2$ + TBHP" protocol was also futile. No formation of aldehyde was detected and the starting alcohol was fully recovered after stirring for 24 h at 45 °C.

Recycling of the 1$-$SiO$_2$ Catalyst and Leaching Studies. The silica gel-supported Ru catalyst has been subjected to eight successive reuses under the reaction conditions: 1-phenyl-1-propanol (1 mmol), **1**$-$SiO$_2$ (600 mg), and TBHP (2.3 mmol) in *n*-hexane at 40$-$45 °C for 14 h. After centrifugation of the reaction mixture, the supernatant solution was decanted to separate the catalyst, which was washed several times with CH$_2$Cl$_2$. The reaction vessel containing the catalyst was recharged with 1-phenyl-1-propanol, TBHP, and *n*-hexane for another consecutive reaction run. The combined supernatant and organic washings were collected for product identification and quantitation. As shown in Table 2, the catalytic activity of **1**$-$SiO$_2$ remained largely unchanged for eight successive runs, and each reaction run could attain >90% alcohol consumption and 99% ketone yield with a total of 690 turnovers being achieved. After eight consecutive reactions, the recovered **1**$-$SiO$_2$ was found to contain 0.94%w/w of Ru based on ICP analysis. This Ru content is essentially the same as the initial value, indicative of no catalyst leaching during the reaction cycles. By using less **1**$-$SiO$_2$ catalyst (120 mg, 1.9 μmol of Ru), 1-phenyl-1-ethanol (10 mmol) reacted with TBHP (23 mmol) in *n*-hexane (20 mL) at 40 °C to afford ethyl phenyl ketone (84% substrate conversion, 99% yield, turnovers = 4366), albeit with longer reaction time of 72 h. Subsequent consecutive run gave similar results (100% alcohol consumption; 99% ketone yields, turnovers = 5129), and up to 9495 turnovers were achieved for two successive reactions.

TABLE 2. Catalyst Recyclability Studies in *n*-Hexane and Dichloromethane



	n-hexane		CH$_2$Cl$_2$	
reaction run	% conversion	% yield	% conversion	% yield
1	93	99	76	97
2	94	99	59	84
3	95	99	62	80
4	93	99	52	97
5	96	99	58	97
6	93	99	58	97
7	95	99	54	97
8	95	99	57	85

Reaction conditions: A mixture containing 1-phenyl-1-propanol (1 mmol), **1**$-$SiO$_2$ (600 mg), and TBHP (2.3 equiv) in either *n*-hexane or CH$_2$Cl$_2$ was stirred at 40$-$45 °C for 14 h. After centrifugation, aliquots were taken from the supernatant liquid for product identification and quantitation using capillary GC. To recycle the supported catalyst, the supernatant liquid was removed from the reaction vessel, followed by washing the catalyst with fresh CH$_2$Cl$_2$ (3 × 10 mL). The reaction vessel containing **1**$-$SiO$_2$ was recharged with fresh alcohol and TBHP for subsequent consecutive reactions.

When CH$_2$Cl$_2$ was used as solvent, lower alcohol consumption was observed for the **1**$-$SiO$_2$ catalyzed 1-phenyl-1-propanol oxidation (see Table 2). The ICP analysis of the recycled catalyst (after the eighth reaction run) revealed the Ru content being 0.92% w/w, which is comparable to the initial value of 0.94%w/w. Using CH$_2$Cl$_2$ as solvent, we noticed that the supported catalyst gradually developed a pink red color upon consecutive reaction runs. The solid diffuse-reflectance UV$-$vis spectrum showed an intense absorption band at $\lambda_{max} = 546$ nm, which is conspicuously absent in the corresponding spectrum of **1**$-$SiO$_2$. This spectral feature resembles to the visible absorption of [(Me$_3$tacn)Ru^{III}(μ-O)(μ-CF$_3$CO$_2$)$_2$-Ru^{IV}(Me$_3$tacn)]$^+$ at $\lambda_{max} = 560$ nm (Supporting Information).[30] We found that the dimeric ruthenium complex exhibits negligible catalytic activity. Treatment of benzyl alcohol (1 mmol) with TBHP (1.2 mmol) and [(Me$_3$tacn)-Ru^{III}(μ-O)(μ-CF$_3$CO$_2$)$_2$Ru^{IV}(Me$_3$tacn)]$^+$ (1 mol %) in CH$_2$Cl$_2$ (5 mL) at room temperature failed to produce benzaldehyde as detected by capillary GC, and the starting alcohol was completely recovered. Therefore, the apparent diminished catalytic activity of **1**$-$SiO$_2$ in CH$_2$Cl$_2$ is presumably due to formation of inactive dimeric ruthenium complex.

Heterogeneous Alkene Epoxidation. Oxidation of Disubstituted Alkenes. As reported earlier, **1** is an effective catalyst for homogeneous epoxidation of alkenes by TBHP. In this work, treatment of norbornene (1 mmol) with TBHP (2.3 mmol, 4.92 M in 1,2-dichloroethane) and **1**$-$SiO$_2$ (600 mg) in CH$_2$Cl$_2$ furnished *exo*-epoxynorbornane exclusively in 96% yield (Table 3). No *endo*-epoxides and other rearranged products such as norcamphor and cyclohexene carboxyaldehyde were detected in the **1**$-$SiO$_2$-

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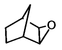
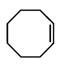
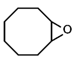
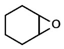
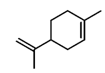
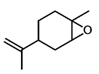
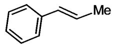
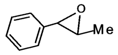
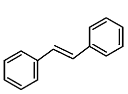
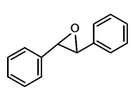
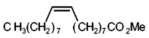
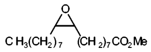
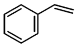
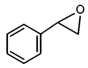
[29] Tidwell, T. T. *Synthesis* **1990**, *10*, 857.

[30] Neubold, P.; Wieghardt, K. Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 933.

TABLE 3. Heterogeneous 1−SiO$_2$ Catalyzed Alkene Epoxidation by TBHP

entry	alkene	%conversion	product	%yield^a
1		100		96
2		100		96
3		78		75
4		100		53^b
5		80		71
6		19		75^c
7		92		67^b
8		78		89^d

Reaction conditions: A mixture of alkene (1 mmol), **1**−SiO$_2$ (600 mg), and TBHP (2.3 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred at room temperature for 14 h. After centrifugation, aliquots were taken from the supernatant liquid for capillary GC analysis with 1,4-dichlorobenzene as internal standard. ^{a} Yields were determined based on %alkene conversion. ^{b} Isolated yield. ^{c} Yield was determined by ^{1}H NMR using 1,1-diphenylethene as internal standard. ^{d} Benzaldehyde (8%) was also detected.

catalyzed reaction. Changing the solvent to *n*-hexane, benzene, or toluene as solvent produced almost identical results.

Likewise, cyclooctene was effectively oxidized to its *exo*-epoxide exclusively (96% yield) under the **1**−SiO$_2$ catalyzed conditions. It is noteworthy that both norbornene and cyclooctene are poor substrates for the TS-1 catalyzed oxidation by H$_2$O$_2$.[31] With cyclohexene as substrate, cyclohexene oxide was formed in 75% yield; 2-cyclohexenone was formed as the side-product in 14% yield. The observed product profile for the heterogeneous cyclohexene oxidation is comparable to that of the analogous homogeneous **1**-catalyzed reactions. It is known that allylic C−H bond oxidation is usually prevailing for cyclohexene oxidation by Ru═O complexes. [17, 18a−h]

Previously we found that the homogeneous **1**-catalyzed (+)-limonene oxidation gave 1,2-epoxide (54%) as major product and terminal 8,9-epoxide as minor product (16% yield).[9d] Nevertheless, the heterogeneous **1**−SiO$_2$ catalyzed reaction afforded 1,2-epoxide as the only isolable product (53% yield) with complete alkene consumption. When the crude reaction mixture was examined by ^{1}H NMR spectroscopy, a complex mixture was observed with the 1,2-epoxide being the only identifiable product. The absence of terminal 8,9-epoxide could be due to epoxide decomposition induced by the surface acidity of the silica support (see later section).

The heterogeneous oxidation of disubstituted aromatic alkenes have been examined. With *trans*-*β*-methylstyrene as substrate, the **1**−SiO$_2$ catalyzed alkene epoxidation proceeded effectively to afford *trans*-*β*-methylstyrene oxide (71%) and benzaldehyde (8%), comparable to previous results for the analogous homogeneous reaction.[9d] Our previous study showed that the **1**-catalyzed *trans*-stilbene oxidation afforded *trans*-stilbene oxide in 54% yield with 62% alkene consumption.[9d] In this work, the heterogeneous *trans*-stilbene oxidation [**1**−SiO$_2$ (600 mg), alkene (1.0 mmol), and TBHP (2.3 mmol) in CH$_2$Cl$_2$] attained only 19% substrate conversion in 14 h, though *trans*-stilbene oxide was produced exclusively in 75% yield. Analogous to the heterogeneous menthol oxidation discussed in earlier section, we propose that the decreased reactivity of *trans*-stilbene could be related to unfavorable steric interaction of the alkene with the silica surface.

We have examined oxidation of methyl 9-*cis*-octadecenoate under the **1**−SiO$_2$-catalyzed conditions. We found that only *cis*-epoxide was selectively produced (67% isolated yield) and no *trans*-epoxide was observed based on ^{1}H NMR analysis of the crude reaction mixture. This high stereoselectivity compares well with a similar reaction using dioxirane as oxidant,[32] whereas the analogous reaction with high valent Ru═O species resulted in considerable formation of *trans*-epoxide products.[17, 18a−h]

Oxidation of Terminal Alkenes. Under the standard reaction conditions, styrene (1 mmol) was effectively oxidized to styrene oxide (89% yield) by TBHP (2.3 mmol) in the presence of **1**−SiO$_2$ (1%w/w, 600 mg) in CH$_2$Cl$_2$ (78% alkene consumption for 8h reaction time; see Table 3, entry 8); benzaldehyde (8%) was also formed. In this case, no phenylacetaldehyde was detected. In attempt to obtain complete alkene consumption, the reaction mixture was left for prolonged stirring for an additional 6 h. Subsequent capillary GC analysis showed that styrene oxide was produced in 46% yield albeit with complete styrene consumption. In contrast, prolonged reaction time has no significant effect on epoxide yields for the analogous norbornene and *trans*-*β*-methylstyrene oxidations.

In view of the lower yield observed for the **1**−SiO$_2$-catalyzed styrene oxidation, the reaction was monitored by capillary GC; the time courses for the respective styrene consumption and styrene oxide formation are represented by curves A and B of Figure 2. During 0−2 h (1st phase) more styrene was consumed (5.8% h^{-1}) than the product epoxide being formed (1.7% h^{-1}) and the benzaldehyde:styrene oxide ratio was found to be 61:14. However, during 3−8 h (2nd phase) the styrene consumption (18% h^{-1}) and styrene oxide formation (16% h^{-1}) proceeded at similar rates, and the maximum epoxide yield of 89% was obtained after 8 h of reaction. From 8 h and beyond (3rd phase), a gradual decrease in styrene oxide was found. This could be attributed to decomposition of styrene oxide by the silica surface acidity, presumably via epoxide ring opening reaction.

Recycling of 1−SiO$_2$ Catalyst and Leaching Studies. Similar to the alcohol oxidations described earlier,

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[31] Murugavel, R.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 477 and references therein.

[32] For reviews of dioxirane chemistry, see: (a) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, 1990; Vol. 2, p 1. (b) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205. (c) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.

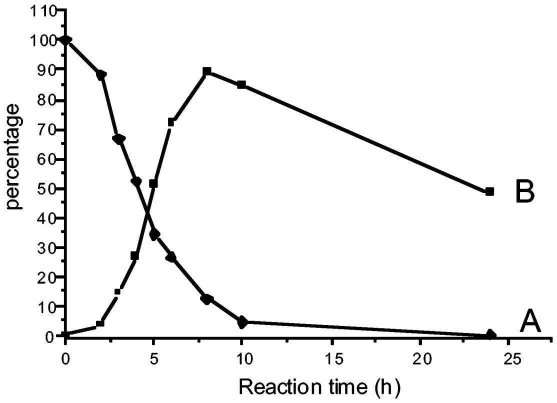


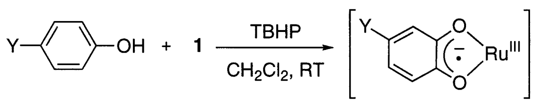
FIGURE 2. Time course for the **1**−SiO_2 catalyzed styrene oxidation. Curve A: styrene consumption; Curve B: styrene oxide formation.

the supported Ru catalyst has been reused for four successive reactions under the reaction conditions: norbornene (1 mmol), **1**−SiO_2 (600 mg), TBHP (2.3 mmol) in *n*-hexane (5 mL) for 12 h at room temperature. The supported catalyst was recycled by centrifugation, followed by removal of the supernatant solution and several washings with CH_2Cl_2. A total of 385 turnovers was attained for four consecutive reactions: first run, epoxide yield = 99%, alkene conversion = 96%, turnovers = 96; second run, epoxide yield = 99%, alkene conversion = 95%, turnovers = 95; third run, epoxide yield = 99%, alkene conversion = 97%, turnovers = 97; fourth run, epoxide yield = 99%, alkene conversion = 97%, turnovers = 97. There is no apparent loss of catalytic activity over four successive catalyst recycling, and the Ru content of the reused supported catalyst was found to be the same as the initial value of 0.94%w/w determined by ICP. On the basis of FT-Raman analysis, the Me_3tacn ligand was probably retained since the characteristic C−H stretches (2900 and 2979 cm^{-1}) were still observed in the recovered **1**−SiO_2 catalyst.

Oxidation of Phenols. Oxidative transformation of phenols to quinones has been a subject of extensive studies due to its biological and synthetic importance.[33] Transition metal catalyzed oxidation of phenols with peroxides is known to proceed nonselectively with formation of various side-products from radical coupling and/or overoxidation products.[34] Murahashi and co-workers had reported that $[Ru^{II}(PPh_3)_3Cl_2]$ can effect oxidation of 4-substituted phenols and derivatives by TBHP to give (*tert*-butyldioxy)cyclohexadienones selectively.[35]

Given that the "**1**−SiO_2 + TBHP" protocol is effective for alcohol and alkene oxidations, we therefore examined its activity toward phenol oxidation. However, when 4-isopropylphenol was treated with **1**−SiO_2 (600 mg) and TBHP (2.3 equiv) in CH_2Cl_2 at room conditions, a dark blue color developed over the silica gel surface within 5−10 min. On the basis of capillary GC analysis, no formation of (*tert*-buthyldioxy)cyclohexadienone and/or other radical coupling/overoxidation products was observed with over 95% recovery of the starting phenol. Similar results [i.e., no formation of (*tert*-butyldioxy)-cyclohexadienone and other phenol oxidation products] were observed when reacting **1** (1 equiv) with 4-isopropylphenol (1.5 equiv) and TBHP (10 equiv) in CH_2Cl_2 at room temperature. Instead, a dark blue species with a characteristic absorption band λ_{max} = 576 nm was formed spontaneously. ESI-MS analysis of the reaction mixture revealed a prominent ion cluster peak at m/z = 536, corresponding to $[(Me_3tacn)Ru^{III}(CF_3CO_2)(C_9H_{11}O_2)]^+$ formulation. The same species can be detected by reacting **1** with 4-isopropylcatechol in CH_2Cl_2, and it showed identical UV−vis and ESI-MS spectral patterns. We tentatively assign this species to be a ruthenium−catecholate complex; attempt to isolate the complex gave an intractable solid that rendered structural characterization difficult.

TABLE 4. Ruthenium-Mediated Oxidation of Phenols by TBHP



entry	Y	UV-vis (nm)	ESI-MS (m/z)
1	iPr	276 (ϵ = 4332 $dm^3\ mol^{-1}\ cm^{-1}$) 576 (ϵ = 1993 $dm^3\ mol^{-1}\ cm^{-1}$)	536
2	Me	271 (ϵ = 5625 $dm^3\ mol^{-1}\ cm^{-1}$) 575 (ϵ = 1020 $dm^3\ mol^{-1}\ cm^{-1}$)	508
3	Ph	325 (ϵ = 1450 $dm^3\ mol^{-1}\ cm^{-1}$) 575 (ϵ = 1640 $dm^3\ mol^{-1}\ cm^{-1}$)	584
4	H	275 (ϵ = 6950 $dm^3\ mol^{-1}\ cm^{-1}$) 563 (ϵ = 3540 $dm^3\ mol^{-1}\ cm^{-1}$)	494

Oxidation of several phenol derivatives by the "**1** + TBHP" protocol has been examined, and Table 4 depicts the relevant UV−vis and ESI-MS data. In this work, formation of the ruthenium−catecholate complex can be regarded as *ortho*-hydroxylation of phenols, analogous to the copper-mediated reaction involving dicopper-peroxo active intermediate.[36]

Experimental Section

Materials. All the solvents and alcohols/alkenes substrates were purified by standard procedure before uses. Cyclohexene, cyclooctene, and styrene were first washed with 10% sodium hydroxide and then distilled over calcium hydride. Norbornene was purified by sublimation, whereas *trans*-stilbene was purified by recrystallization before use. *tert*-Butyl hydroperoxide, obtained commercially as a 70% aqueous solution, was pretreated by the procedure described by Sharpless and coworkers using 1,2-dichloroethane and was later standardized by ^1H NMR (4.92 M in 1,2-dichloroethane).[21]

Preparation of $[(Me_3tacn)Ru(CF_3CO_2)_2(H_2O)]CF_3CO_2$ (1). A modified procedure was employed. $[(Me_3tacn)RuCl_3]$ (1.0 g, 2.54 mmol) was heated at reflux with silver trifluoromethanesulfonate (1.92 g, 7.6 mmol) in trifluoroacetic acid

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[33] (a) Hudlicky, M. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, D. C. 1990; p 163. (b) Whiting D. A. In *Comprehensive Organic Chemistry*; Stoddart, F., Ed.; Pergamon: Oxford, 1979; Vol. 1, p 707. (c) Harborne, J. B. *Biochemistry of Phenolic Compounds*; Academic Press: London, 1964. (d) Pridham, J. B. *Enzyme Chemistry of Phenolic Compounds*; Pergamon: New York, 1963.

[34] (a) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. 1, p 37. (b) Taylor, W. I.; Battersby, A. R. *Oxidative Coupling of Phenols*; Marcel Dekker: New York, 1967.

[35] Murahashi, S.-I.; Naota, T.; Miyaguchi, N.; Noda, S. *J. Am. Chem. Soc.* **1996**, *118*, 2509.

[36] Examples for phenol oxidation by peroxo-copper complexes to form discrete catechol intermediates, see: (a) Mandal, S.; Macikenas, D.; Protasiewicz, J. D.; Sayre, L. M. *J. Org. Chem.* **2000**, *65*, 4804. (b) Berreau, L. M.; Mahapatra, S.; Halfen, J. A.; Houser, R. P.; Young, V. G., Jr.; Tolman, W. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 207.

(0.2 M, 125 mL) for 0.5 h. During this time, the starting ruthenium complex dissolved to give a pale red solution with formation of AgCl precipitate. The reaction mixture was filtered, and the volume was reduced slowly by evaporation at 70 °C to ca. 20 mL. Any insoluble solid was removed by filtration to give a pale red solution. The solution was left standing at room temperature for several days to afford the product complex as a yellow microcrystalline solid. Additional crops of the product could be obtained by further slow evaporation of the reaction mixture. Yield of the solid: 0.82 g (52%).[9c] Anal. Calcd for $C_{15}H_{23}F_9N_3O_7Ru$: C, 28.62; H, 3.68; N, 6.68. Found: C, 28.94; H, 3.53, N, 6.33. FAB-MS: $m/z = 499$ [$M^+ - H_2O - CF_3CO_2$], 385 [$M^+ - H_2O - 2CF_3CO_2$]. FT-IR: 1713 ($\nu_{C=O}$).

Preparation of the Silica Gel-Supported Ruthenium Catalyst, 1−SiO₂. Silica gel (5.940 g, Merck Kieselgel, 230−400 mesh ASTM, preheated at 110 °C for overnight to remove moisture) was added to an ethanolic solution (50 mL of absolute ethanol) of **1** (60 mg, 10 μmol) with continuous stirring at room temperature. The solvent was removed by rotary evaporation at 40 °C to afford a pale yellow powder solid, which was further dried in a vacuum at room temperature for overnight. The solid was kept under a nitrogen atmosphere to avoid contact with moisture.

Determination of the Ru Content in 1−SiO₂. The silica-supported Ru-catalyst (208.8 mg) was extracted with concentrated HCl (5 × 2 mL) in a screw-capped vessel to give a pale yellow solution. The combined acid solutions containing the Ru complex were evaporated by heating to ca. 1 mL, followed by treatment with concentrated nitric acid (2 mL) to digest the metal complex. Removal of the nitric acid by heating gave a red-brown residue, which was dissolved in deionized water (3 × 1 mL) and transferred to a volumetric flask (5.0 mL) for ICP analysis. The Ru concentration was determined by measuring the atomic emission (240.2 nm) with reference to a linear ($R = 0.99$) calibration curve of (0.26−1.3 mM) **1** prepared in a manner identical to the sample preparation.

General Procedure for the 1−SiO₂-Catalyzed Alcohol Oxidation. To a screw-capped vessel was charged with a mixture of alcohol (1 mmol), **1**−SiO_2 (600 mg, 1%w/w), and TBHP (2.3 mmol) in *n*-hexane (5 mL). After stirring at 45 °C for 14 h, the reaction mixture was centrifuged, and the aliquots were taken from the supernatant liquid for product identification and quantitation using capillary GC analysis.

To obtain the products, the supernatant liquid was separated, and the catalyst was washed with CH_2Cl_2 (3 × 10 mL). The combined supernatant liquid and washings were then evaporated to dryness by rotary evaporation, and the residue was loaded onto a silica gel column for chromatographic purification.

General Procedure for the 1−SiO₂-Catalyzed Alkene Oxidation. To a screw-capped vessel was charged with a mixture of alkene (1 mmol), **1**−SiO_2 (600 mg, 1%w/w), and TBHP (2.3 mmol) in CH_2Cl_2/*n*-hexane (5 mL). After stirring at room temperature for 14 h (except for styrene), the reaction mixture was centrifuged, and the aliquots were taken from the supernatant liquid after addition of internal standard (1,4-dichlorobenzene) for capillary GC analysis. For *trans*-stilbene oxidation, the supernatant liquid was separated, and the Ru catalyst was washed repeatedly (3 × 10 mL) with CH_2Cl_2. The combined supernatant liquid and washings were evaporated to dryness by rotary evaporator. After addition of 1,1-diphenylethene as internal standard, the residue was dissolved in $CDCl_3$ for ^{1}H NMR analysis. The amount of *trans*-stilbene oxide was determined by comparing its integral ratio at (δ_H 3.8 ppm) with that at (δ_H 5.4 ppm) of 1,1-diphenylethene.

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Supporting Information Available: Detailed experimental for the X-ray structure determination of complex **1**, crystal data and structure refinement, bond distances and angles, atom coordinates and isotropic displacement parameters, solid diffuse reflectance UV spectra of silica gel, and recovered **1**−SiO_2 with CH_2Cl_2 as solvent for oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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