

Polystyrene-Supported (Catecholato)oxorhenium Complexes: Catalysts for Alcohol Oxidation with DMSO and for Deoxygenation of Epoxides to Alkenes with Triphenylphosphine

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Polymer-supported catalysts offer practical advantages for organic synthesis, such as improved product isolation, ease of catalyst recycling, and compatibility with parallel solution-phase techniques. We have developed the (carboxypolystyrene-catecholato)rhenium catalyst **2** derived from tyramine (=4-(2-aminoethyl)phenol), which is effective for alcohol oxidation with dimethylsulfoxide (DMSO) and for epoxide deoxygenation with triphenylphosphine. The supported [Re(catecholato)]catalyst **2** is air- and moisture-stable and can be recovered and used repeatedly without decreasing activity. The procedures work with non-halogenated solvents (toluene). DMSO for Re-catalyzed alcohol oxidation is inexpensive and safer for transport and storage than commonly used peroxide reagents. The oxidation procedure was best suited for aliphatic alcohols, and the mild conditions were compatible with unprotected functional groups, such as those of alkenes, phenols, nitro compounds, and ketones (see *Tables 1* and *2*). Selective oxidation of secondary alcohols in the presence of primary alcohols was possible, and with longer reaction time, primary alcohols were converted to aldehydes without overoxidation. Epoxides (oxirans) were catalytically deoxygenated to alkenes with this catalyst and Ph₃P (see *Table 3*). Alkyloxiranes were converted to the alkenes with retention of configuration, while partial isomerization was observed in the deoxygenation of *cis*-stilbene oxide (*cis*-1,2-diphenyloxirane). These studies indicate that supported [Re(catecholato)] complexes are effective catalysts for O-atom-transfer reactions, and are well suited for applications in organic synthesis.

Introduction. – The development of supported catalysts is an area of great interest and offers numerous practical applications in organic synthesis. Several excellent review articles on the topic of supported catalysts in organic chemistry have recently appeared [1–7]. The use of polymer-supported ligands for modifying homogeneous metal-catalyzed reactions to operate as heterogeneous systems provides significant advantages, *e.g.*, simple product isolation and the possibility of catalyst recycling. This approach has been highly successful for catalytic reductions, oxidations, and C–C bond forming reactions [1–7]. The use of supported chiral ligands for enantioselective C–C bond forming reactions is an area of particular importance [8–15].

The oxidation of alcohols to aldehydes or ketones is a fundamental transformation that remains an active area of research because of the increasing demand for processes that involve safe, economical reagents, avoid hazardous solvents, minimize waste by-

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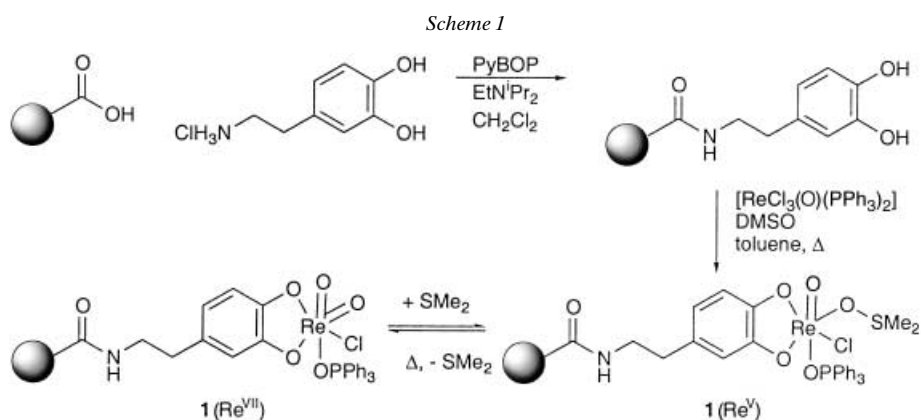
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products, and satisfy requirements for chemoselectivity. Polymer-supported reagents/catalysts for alcohol oxidation are particularly important for applications in parallel solution-phase synthesis, where product purification can be facilitated by simple filtration. Recently, a derivative of the widely used periodinane oxidant 2-iodoxybenzoic acid was rendered heterogeneous by attachment to a polystyrene support, and this reagent was used for the oxidation of various alcohols [16]. Immobilized 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) nitroxyl radicals were shown to be efficient catalysts for alcohol oxidation with hypochlorite, and preferential selectivity for primary alcohols in the presence of secondary alcohols was exhibited [17–19]. A polymer-bound bromite reagent was used for alcohol oxidation together with a catalytic amount of TEMPO [20]. A variety of polymer-supported transition metal complexes have been used for alcohol oxidation. Chlorochromate imidazolium reagents, *e.g.*, oxidized benzylic and allylic alcohols [21]. Polystyrene-supported $[\text{Co}^{\text{II}}(\text{PPh}_3)]$ catalyzed the oxidation of benzylic and allylic alcohols with *tert*-butyl hydroperoxide, but was not effective for aliphatic alcohols [22]. A related system using a supported (phosphine)ruthenium complex with *t*-BuOOH oxidized aliphatic alcohols and hydrocarbons to ketones, and also catalyzed transfer hydrogenation from propan-2-ol [23]. Polymer-supported perruthenate efficiently catalyzed the oxidation of primary and secondary benzylic alcohols, but did not oxidize secondary aliphatic alcohols [24–27]. Polymer-supported 4-methylmorpholine *N*-oxide has been used as the co-oxidant in the perruthenate-catalyzed oxidation of alcohols [28].

Rhenium complexes catalyze a variety of synthetically useful reactions, and a great deal of interest has focused on homogeneous peroxide/methyltrioxorhenium ($[\text{Re}(\text{Me})\text{O}_3]$; MTO) catalyzed oxidations [29–33]. Recently, a heterogeneous poly(4-vinylpyridine)/MTO/ H_2O_2 system was used for the catalytic epoxidation of alkenes [34]. Our laboratory has investigated a variety of homogeneous Re^{V} -catalyzed O-atom-transfer reactions using sulfoxides as O-donors [35–37]. Sulfoxides such as DMSO are readily-available, economical, and stable oxidants. The *Swern* oxidation of alcohols relies on DMSO but requires anhydrous solvents, low temperatures, an amine base, and a stoichiometric amount of a strong electrophilic activating agent, *e.g.*, oxalyl chloride [38]. Sulfoxides are also effective oxo-transfer agents capable of producing oxometal complexes; however, few examples of transition-metal-catalyzed alcohol oxidations with sulfoxides have been reported, and most are limited to easily oxidizable benzylic and allylic substrates [39–41]. We recently reported a rhenium-catalyzed alcohol oxidation with methylsulfoxide in ethylene glycol/toluene, which produced the corresponding ketals in high yields [42]. The presence of ethylene glycol was required for the generation of an active catalyst, which suggested the possible *in situ* formation of a rhenium complex containing a coordinated diol ligand. Subsequent studies in our laboratory have investigated catechols (benzene-1,2-diols) as potential ligands for rhenium-catalyzed alcohol oxidation with DMSO, and we found that 5% $[\text{ReCl}_3(\text{O})(\text{PPh}_3)_2]$ /catechol/DMSO was an efficient homogeneous system for alcohol oxidation [43]. These results led us to investigate polymer-supported (catecholato)-rhenium complexes as heterogeneous catalysts for O-transfer reactions. Herein, we describe the synthesis of a polystyrene-supported Re catalyst with a tyramine-derived ligand (tyramine = 4-(2-aminoethyl)phenol) and report synthetically useful applica-

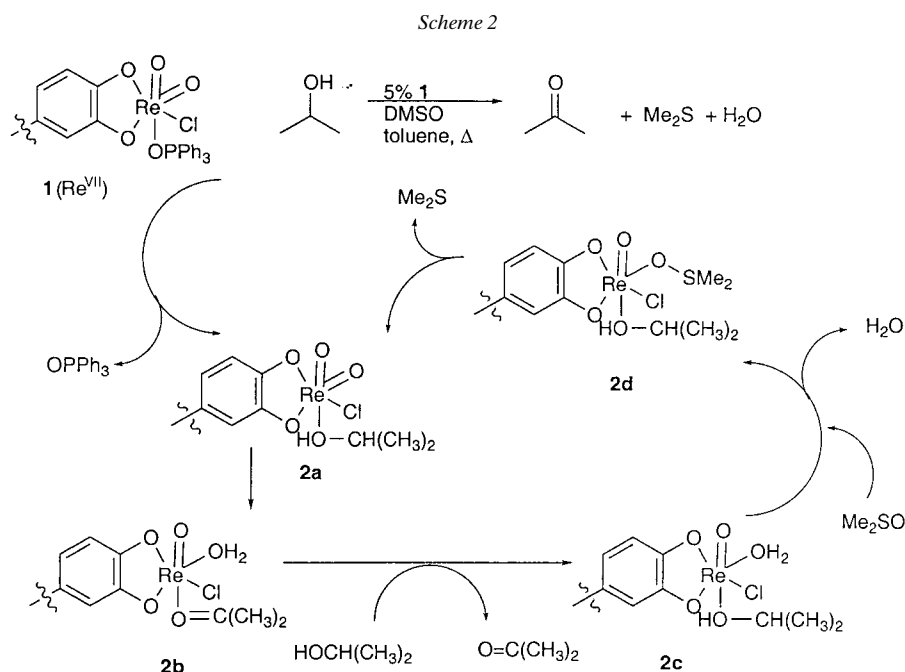
tions for the oxidation of alcohols with DMSO, as well as the reduction of epoxides to alkenes with PPh_3 .

Results and Discussion. – *Polymer-Supported Rhenium Catalyst.* The immobilized catecholato ligand was prepared by coupling 3-hydroxytyramine to commercially available carboxypolystyrene (*Novabiochem*, 100–200 mesh, 1% divinylbenzene, loading capacity 1.24 mmol g^{-1}) in the presence of (1*H*-benzotriazol-1-yloxy)tri(pyrrolidin-1-yl)phosphonium hexafluorophosphate (PyBOP) and EtN^iPr_2 in CH_2Cl_2 (*Scheme 1*). The course of the reaction was monitored by FT-IR by observing the disappearance of the carboxy absorbance at 1688 cm^{-1} . The resulting polystyrene-supported catechol was allowed to react with the oxorhenium complex $[\text{ReCl}_3(\text{O})(\text{PPh}_3)_2]$ and DMSO in toluene, and heated to reflux for 1 h. The polymer-supported (catecholato)rhenium complex **1** was isolated by filtration, and the resin rinsed thoroughly with CH_2Cl_2 . It exhibited a strong IR absorbance at 908 cm^{-1} , characteristic of the $\text{Re}=\text{O}$ oxo group. The complex retained a triphenylphosphine oxide ligand (*vide infra*), and the FT-IR spectra were consistent with a (monochloro)-(monooxo)rhenium(V) complex containing a coordinated sulfoxide ligand. Dimethylsulfide was produced when the polymer complex was heated in refluxing toluene and is expected to produce the corresponding dioxorhenium(VII) complex. The structures of several (catecholato)rhenium [44–46] and bis(catecholato) complexes [47–49] have been reported, and **1** (Re^{V}) is closely related to the known complex $[\text{ReCl}(\text{C}_6\text{H}_4\text{O}_2)(\text{O})(\text{PPh}_3)_2]$ by substitution of the phosphine ligands with a phosphine oxide and sulfoxide ligand [45]. Ongoing studies with simple catecholato ligands are currently in progress in our laboratory and are expected to provide more detailed structural information.



Alcohol Oxidation. The polymer-bound complex **1** was found to be an active catalyst for the oxidation of propan-2-ol with DMSO, producing acetone, H_2O , and Me_2S , as shown in *Scheme 2*. A small amount of triphenylphosphine oxide, corresponding to the quantity of polystyrene-supported Re -complex **1**, was also released as a labile ligand from the original complex during the alcohol oxidation reaction, and was

isolated in the filtrate from the reaction mixture. A working hypothesis for the catalytic cycle of this reaction is shown in *Scheme 2*. The (alcohol)rhenium(VII)dioxo complex **2a** undergoes oxidation of the secondary-alcohol C–H to produce the (ketone)rhenium(V) complex **2b**. Displacement of the labile ketone and H₂O ligands by additional alcohol and DMSO would form **2d**. Oxidation of Re^V to Re^{VII} by the coordinated sulfoxide ligand would then generate **2a** and resume the cycle. The polystyrene-supported complex **2** isolated from the propan-2-ol oxidation retained its catalytic activity for alcohol oxidation and was stable to storage at room temperature for months without observable decomposition. Subsequent oxidations of propan-2-ol using recovered **2** proceeded equally well under these conditions. The product was free from additional triphenylphosphine oxide, a significant advantage for preparative purification. These results led us to treat the catalyst **1** with propan-2-ol in refluxing toluene as a standard protocol to produce catalyst **2**, which was investigated next.



A variety of alcohols were oxidized in good to excellent yields in the presence of polymer-supported catalyst **2**, as shown in *Table 1*. A typical procedure involved refluxing a 0.2M solution of alcohol substrate in toluene with 5% of catalyst **2** and 1.5 equiv. of DMSO. The removal of H₂O was facilitated by a *Dean-Stark* trap. No precautions to exclude air were necessary. The products were isolated by filtration to remove the heterogeneous catalyst, followed by an aqueous wash to remove DMSO. Secondary alcohols were oxidized at significantly faster rates than primary ones, as shown by comparing the times required for complete oxidation of dodecan-1-ol and -2-ol (*Entries 1 and 2*). The oxidation of dodecan-2-ol was repeated eight times with the

same batch of recovered catalyst, and no decrease in yield or increase in reaction time was observed. The secondary-alcohol moiety was preferentially oxidized in 2,2,4-trimethylpentane-1,3-diol (*Entry 3*). This selectivity for secondary alcohols complements available methods such as TEMPO and TPAP that oxidize primary alcohols preferentially [50]. Primary alcohols were converted to the corresponding aldehydes after longer reaction times, without formation of other common oxidation products such as carboxylic acids. The faster rate of secondary-alcohol oxidation is consistent with a rate determining oxidation of a metalloester intermediate. Isolated alkenes were not oxidized under these conditions, as shown by *Entry 5*. This chemoselectivity in the presence of DMSO is advantageous, since alkene oxidation frequently competes with alcohol oxidation in catalytic metal/peroxide systems. The oxidation of (–)-menthol gave an isolated product that consisted of a 2 : 1 mixture of menthone/isomenthone in 75% yield. This result indicates that partial epimerization at the stereogenic α -center occurred. The epimerization can be attributed to the *Lewis* acidity of the $\text{Re}^{\text{V/VII}}$ complexes involved in the catalytic cycle. The secondary-alcohol functions of the steroids dihydrocholesterol and β -estradiol were oxidized to the corresponding ketones in excellent yields (*Entries 7 and 8*).

A series of benzylic alcohols and cinnamyl alcohol were oxidized under the same reaction conditions, and the results are shown in *Table 2*. Benzyl alcohol was oxidized more rapidly than primary aliphatic alcohols, and benzaldehyde was isolated in 90% yield (*Entry 1*). Small amounts of dibenzyl ether were also isolated from this substrate. The 4-nitro derivative was oxidized completely to the corresponding aldehyde (*Entry 2*). Benzoin (1,2-diphenyl-2-hydroxyethanone) was rapidly oxidized to benzil (diphenylethanedione) in excellent yield (*Entry 5*). The oxidation of the secondary benzylic alcohol benzhydrol (diphenylmethanol) produced only 19% of the expected ketone and was accompanied by formation of the corresponding ether as the major reaction product (*Entry 3*). The oxidation of 1,2-diphenylethanol similarly produced only 17% of the ketone, and stilbene was isolated as the major product from a competing elimination reaction (*Entry 4*). These results can be attributed to the mildly acidic conditions of the oxidation, which can initiate the generation of benzylic carbocations and lead to ether formation or elimination to alkene products. This explanation is consistent with the absence of ether products in the reactions of benzylic alcohols possessing electron-withdrawing groups that would destabilize the intermediate cation (*Entries 2 and 5*). The oxidation of cinnamyl alcohol produced the aldehyde in 36% yield (*Entry 6*). Small amounts of the ketone produced from the rearranged secondary allylic alcohol and large amounts of ether products were also formed. These observations can be explained by side reactions of allylic alcohols under acidic conditions, where allyl cations are possible intermediates.

Epoxide Reduction. The successful oxidation of alcohols with the polystyrene-supported oxorhenium catalyst **2** and DMSO led us to investigate the possibility of catalyzing other synthetically useful O-atom-transfer reactions. The reduction of epoxides is an important reaction, and a variety of reagents have been developed [51]. The O-transfer reaction of an epoxide to triphenylphosphine is enthalpically very favorable [52]; however, direct reaction does not occur in the absence of a catalyst such as methyltrioxorhenium [53].

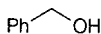

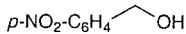
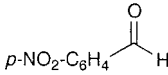
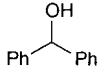

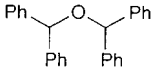
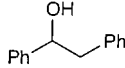
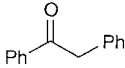
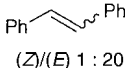
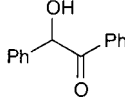
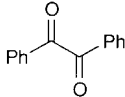
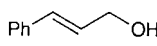
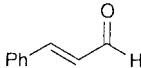
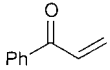
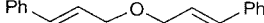
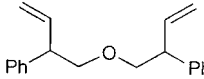
Table 1. (*Polystyrene-Catecholato*)rhenium-Promoted Oxidation of Alkyl Alcohols with DMSO^{a)}

Entry	Substrate	Time [h]	Product	Yield [%]
1		15		98
2		3.5		98
3		0.5		83
4		15		82
5		4		93
6		8		75
7		7		97
8		4		98

^{a)} Alcohol (1 mmol), DMSO (1.5 mmol), Re-catalyst **2** (0.05 mmol), toluene (5 ml), Δ.

The series of epoxides (oxiranes) shown in *Table 3* were reduced to the corresponding alkenes with 1 equiv. of Ph₃P and 5% of catalyst **2** in refluxing toluene. The yields were good to excellent, and the reactions proceeded to completion without requiring the exclusion of O₂. Control experiments demonstrated that no deoxygenation of *trans*-stilbene oxide (*trans*-1,2-diphenyloxirane) by Ph₃P occurred after refluxing

Table 2. (*Polystyrene-Catecholato*)rhenium-Promoted Oxidation of Benzylic and Allylic Alcohols with DMSO^a)

Entry	Substrate	Time [h]	Product(s)	Yield [%]
1		2		90
2		3.5		99
3		0.5		19
				77
4		1.5		17
			 (<i>Z</i>)/(<i>E</i>) 1 : 20	82
5		0.5		93
6		1		36
				5
				36
				18

^a) Alcohol (1 mmol), DMSO (1.5 mmol), Re-catalyst **2** (0.05 mmol), toluene (5 ml), Δ .

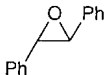
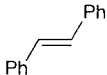
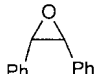
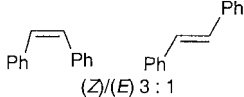
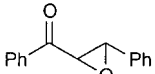
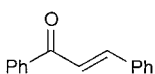
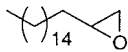
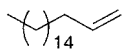
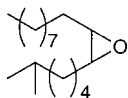
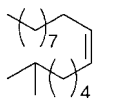
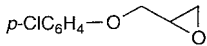
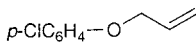
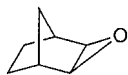

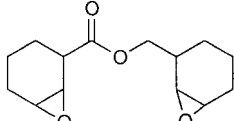
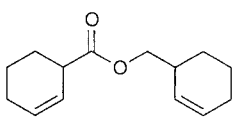
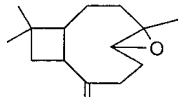
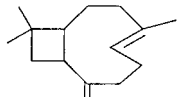
for 24 h in the absence of **2**. Phenyloxiranes reacted more rapidly than alkyloxiranes (*Entries 1–3*). Similar reaction times were required for complete conversion of *cis*- and *trans*-stilbene oxide. The deoxygenation of *trans*-stilbene oxide produced (*E*)-stilbene in 92% yield, with complete retention of configuration, while *cis*-stilbene oxide produced a 3:1 mixture of the (*Z*)/(*E*)-stilbene stereoisomers. A control reaction in which (*Z*)-stilbene was subjected independently to the reaction conditions demon-

strated that none of the (*E*)-stereoisomer was produced, which indicates that the (*Z*) → (*E*) isomerization occurs during the deoxygenation process. The deoxygenation of *trans*-stilbene oxide was conducted repeatedly with the recovered catalyst, and no decrease in yield or increase in reaction time was observed. The reduction of a *cis*-dialkyloxirane produced the (*Z*)-alkene with retention of configuration (*Entry 5*). The terminal epoxide 1,2-epoxyoctadecane (hexadecyloxirane) was completely deoxygenated within 6 h (*Entry 4*). The reaction of 4-chlorophenyl glycidyl ether ([4-chlorophenoxy)methyl]oxirane) was significantly slower (*Entry 6*), and the alkene product was isolated in moderate yield. Polycyclic di- and trisubstituted aliphatic oxiranes were efficiently deoxygenated with this procedure (*Entries 7–9*). Our method is efficient and does not require excess phosphine for complete conversion. Product purification requires only the removal of triphenylphosphine oxide, which can be accomplished by filtration over a small amount of silica gel.

A possible mechanism for the Re-catalyzed epoxide deoxygenation is shown in *Scheme 3*. The cycle begins by coordination of an epoxide **3** to form a [Re^V(catecholato)] complex **4a**. This species then undergoes C–O epoxide-bond cleavage to produce the dialkoxyrhenium(V) (glycolato)(rhenium) complex **4b**. Precedence for this step has been established in previous studies of the deoxygenation of epoxides with methyltrioxorhenium and related cyclopentadienyl and tri(pyrazolyl)borate derivatives [53–55] and in the stereospecific catalytic deoxygenation of diols to alkenes with [Re(Cp*)(O)₃] and Ph₃P [56]. Alkene extrusion from **4b** would produce the [Re^{VII}(O)₂] complex **1**. Alternatively, the epoxide complex **4a** could undergo a direct abstraction of the O-atom to produce **1**. Reduction of the (catecolato)dioxorhenium(VII) complex **1** with triphenylphosphine would then produce the Re^V complex and resume the cycle. A phenyl substituent (R = C₆H₅) would be expected to facilitate both of the C–O bond-breaking steps, leading to the observed rate enhancement for phenyloxiranes. The isomerization observed with *cis*-stilbene oxide might occur during either the C–O bond-breaking step that produces the glycolato complex, or during the subsequent extrusion of the alkene. This isomerization may result from an asynchronous C–O bond-breaking process that involves cationic or radical intermediates capable of rotating around the C–C bond. These steps would be analogous to the acid-mediated side reactions observed during the oxidation of benzylic and allylic alcohols. The extrusion of alkenes from related [Re(Cp*)(1,2-diphenylethane-1,2-diolato)(O)] complexes has been suggested to involve nonsymmetric transition states and stepwise cleavage of the C–O bonds, possibly involving a metallaoxetane intermediate [57]. The retention of configuration observed in the deoxygenation of the *cis*-dialkyloxirane (*Entry 5*) is consistent with a synchronous process that does not involve intermediates with free rotation around the C–C bond. The faster rate of reaction for the simple monoalkyloxirane (*Entry 4*) compared to the glycidyl derivative (*Entry 6*) may reflect the ability of the additional O-atom to coordinate the metal, or alternatively this group may play a role in the destabilization of the C–O bond-breaking process through inductive effects. Further investigations using isolated catecholato complexes to elucidate mechanistic details of this reaction are currently in progress.

Conclusions. – In summary, we have successfully developed a polymer-supported rhenium catalyst for alcohol oxidation and epoxide deoxygenation. The carboxypoly-

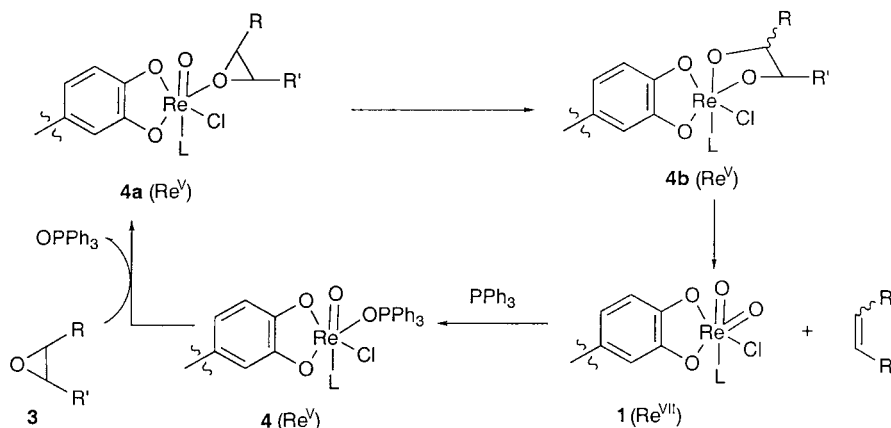
Table 3. (*Polystyrene-Catecholato*)rhenium-Promoted Epoxide Reduction with $\text{Ph}_3\text{P}^{\text{a}}$

Entry	Substrate	Time [h]	Product	Yield [%]
1		1.5		92
2		1.5	 (Z)/(E) 3 : 1	90
3		4		92
4		6		97
5		10		91
6		16		60
7		8		92
8		8		82
9		7		90

^a) Epoxide (1 mmol), Ph_3P (1 mmol), Re-catalyst **2** (0.05 mmol), toluene (5 ml), Δ .

styrene-supported tyramine derivative was easily synthesized and proved to be an effective heterogeneous ligand for the formation of stable (catecholato)rhenium complexes. The supported $[\text{Re}(\text{catecholato})]$ catalyst **2** was air- and moisture-stable and could be recovered and used repeatedly without loss of activity. The alcohol oxidation procedure uses DMSO, which is inexpensive and safer for transport and storage than commonly used peroxide reagents. This oxidation procedure was best suited for aliphatic alcohols, and the mild conditions were compatible with unprotected functional groups found in alkenes, phenols, nitro compounds, and ketones. Selective

Scheme 3



oxidation of secondary alcohols in the presence of primary alcohols was possible, and with longer reaction time, primary alcohols were converted to aldehydes without overoxidation. Epoxides were catalytically deoxygenated to alkenes with catalyst **2** and Ph_3P . Alkyloxiranes were converted to the alkenes with retention of configuration, while partial isomerization was observed with *cis*-stilbene oxide. The workup and purification procedures of these heterogeneous Re-catalyst-promoted transformations involve simple filtration, and the catalyst could be recovered and used repeatedly without loss of activity. These studies indicate that supported [Re(catecholato)] complexes are effective catalysts for O-atom-transfer reactions and are, thus, well-suited in organic synthesis.

Experimental Part

General. Reagent chemicals were used as obtained commercially without further purification. Carboxy-polystyrene HL (100–200 mesh, 1% DVB; substitution: 1.24 mmol/g) and PyBOP were purchased from *Novabiochem*. Alcohol and epoxide substrates, reagents, and deuterated solvents were purchased from *Aldrich*, toluene and CH_2Cl_2 from *Fischer*, and potassium perrhenate from *Johnson-Matthey*. The starting complex $[ReCl_3(O)(PPh_3)_2]$ was prepared following the literature procedure [58]. Column chromatography (CC): silica gel 60, 70–230 mesh, from *Aldrich*. GC: *Varian 3700*, *Cyclodexb* column (length 30 m, i.d. 0.25 mm, 0.25 μm); samples as hexane solns. IR Spectra: *Perkin-Elmer 1720X FTIR*; KBr pellets; in cm^{-1} . NMR Spectra: *Varian Gemini-200-Fourier-transform* spectrometer; at r.t. (18–22°) in $CDCl_3$; 1H spectra referenced to $SiMe_4$; $^{13}C\{^1H\}$ spectra (at 50 MHz) to the known solvent signals; δ in ppm, coupling constants *J* in Hz.

Polymer-Supported Catechol. To a suspension of carboxypolystyrene HL (500 mg, 0.62 mmol) in CH_2Cl_2 (100 ml) was added PyBOP (967.8 mg, 1.86 mmol), followed by 3-hydroxytyramine hydrochloride (587.9 mg, 3.1 mmol) and EtN^iPr_2 (1.20 g, 9.28 mmol). The mixture was stirred for 72 h at r.t. The mixture was filtered, and the solid was washed sequentially with three portions each of H_2O , MeOH, and CH_2Cl_2 . The solid was dried *in vacuo*: polystyrene- $CONHCH_2CH_2C_6H_3(OH)_2$ (=4-[2-[(polystyrene)carbonyl]amino]ethyl]benzene-1,2-diol; 580 mg). IR: 1604.

Polymer-Supported Rhenium Catalyst 2. To a suspension of polystyrene- $CONHCH_2CH_2C_6H_3(OH)_2$ (500 mg) in toluene (250 ml), $[ReCl_3(O)(PPh_3)_2]$ (833 mg, 1 mmol) was added, followed by anh. DMSO (425 μl , 6 mmol). The mixture was heated under reflux for 1 h. The solid was filtered, washed with three portions of CH_2Cl_2 , and then dried *in vacuo*: 715 mg of **1**. IR: 1604, 908.

A mixture of complex **1** (390 mg), propan-2-ol (1 ml), and toluene (20 ml) was heated under reflux for 1 h. The solid was filtered, washed with three portions of CH₂Cl₂, and dried *in vacuo*: 350 mg of **2**. IR: 1604, 908.

Alcohol Oxidation: General Procedure. The alcohol substrate (1 mmol), catalyst **2** (94 mg, ca. 0.05 mmol of Re), DMSO (110 µl, 1.5 mmol), and toluene (5 ml) were heated under reflux in a flask equipped with a *Dean-Stark* apparatus. The progress of the reaction was monitored by TLC, and heating was continued for the time specified in *Tables 1* and *2*. The mixture was cooled to r.t. and the catalyst removed by filtration and washed with three portions of CH₂Cl₂. The org. layer was washed with H₂O, dried (Na₂SO₄), and evaporated. Products were identified by comparison of ¹H- and ¹³C{¹H}-NMR spectra with authentic material.

Deoxygenation of Epoxides: General Procedure. The epoxide substrate (1 mmol), Ph₃P (1 mmol), and catalyst **2** (94 mg, ca. 0.05 mmol of Re) in toluene (5 ml) were heated to reflux. The progress of the reaction was monitored by TLC or GC, and heating was continued for the time described in *Table 3*. The mixture was cooled to r.t. and the catalyst was removed by filtration and washed with three portions of CH₂Cl₂. The org. layer was concentrated and the residue purified by CC (SiO₂; AcOEt/hexane 1:9). Products were identified by comparison of ¹H- and ¹³C{¹H}-NMR spectra with authentic material.

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