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Dirhodium(II)-Catalyzed Sulfide Oxygenations: Catalyst Removal by Coprecipitation with Sulfoxides

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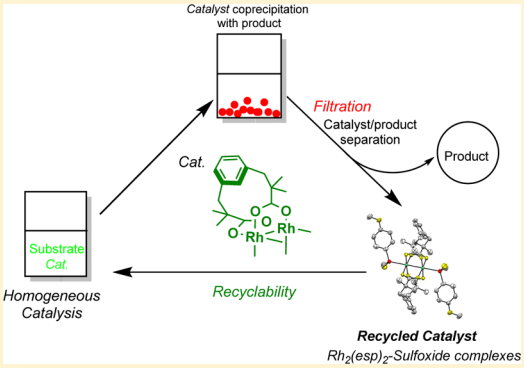
Supporting Information

ABSTRACT: The dirhodium(II) carboxylate complex $Rh_2(esp)_2$ (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropanoate) was shown to catalyze the sulfoxidation of organic sulfides using *tert*-butyl hydroperoxide as the oxidant. Due to the unique structure of $Rh_2(esp)_2$ and its stable $Rh_2(II,II)$ catalyst resting state, the rhodium catalyst is able to precipitate as a $Rh_2(esp)_2$–sulfoxide complex following the reaction which makes separation of the catalyst from the products very convenient. The precipitated $Rh_2(esp)_2$–sulfoxide complexes could be reused to catalyze sulfide oxygenation reactions without considerable loss of activity. Mechanistic studies suggest that the axial ligands fine-tune the redox potential of the dirhodium(II,II) compounds and determine the predominant catalyst species in the oxidation reaction.



INTRODUCTION

Homogeneous transition metal catalysts are extensively used in organic chemistry because of their ability to catalyze important synthetic transformations.[1] However, to use these types of catalysts in industry, thermal stability, and recyclability of catalysts are needed because many industrial scale processes occur at high temperatures and on a large scale.[2] Therefore, metal catalyst recovery methods that are environmentally friendly and efficient are required.[3] We previously found that dirhodium(II) catalyst $Rh_2(esp)_2$ was able to catalyze allylic oxidation reactions using aqueous TBHP (70% *tert*-butyl hydroperoxide in water, T-HYDRO) with a remarkably low catalyst loading.[4,5] Because this catalyst is highly resistant to oxidative degradation, it was able to be recycled and reused in consecutive runs even though the reaction occurred under strongly oxidizing conditions. While Doyle's dirhodium(II) catalyst $Rh_2(cap)_4$ have been shown to undergo one-electron oxidative mechanisms,[6] mechanistic studies for $Rh_2(esp)_2$ suggested a stable dirhodium(II,II) species as the catalyst resting state rather than an unstable dirhodium(II,III) species.[5] The dirhodium(II,II) species is less prone to decomposition which is advantageous in catalysis (Figure 1).

This paper presents a new application for the $Rh_2(esp)_2$-based catalytic oxidation system in the highly selective oxidation of organic sulfides to their corresponding sulfoxides. This organic transformation is of synthetic interest because sulfoxides are common functionalities in the syntheses of pharmaceuticals, agrochemicals, and other fine chemicals.[7] In this work, conditions were optimized for this catalytic reaction with $Rh_2(esp)_2$ and a catalyst removal method was explored. The catalyst precipitated from the reaction mixture as $Rh_2(esp)_2$–sulfoxide complexes, and the catalyst was then removed by filtration. This convenient and efficient catalyst separation method is a promising result to perform this reaction on an industrial scale. By separating the catalyst from the products, there is also a possibility to reuse the dirhodium(II) catalyst in subsequent reactions.[8] These results are ascribed to the unique structure of the dirhodium(II) complex which consists of a binuclear core surrounded by four equatorial μ_2-ligands and two axial ligands (Figure 2).[9]

RESULTS AND DISCUSSION

To optimize the reaction conditions for the oxidation of sulfides, methyl phenyl sulfide **1a** was chosen as a sample substrate. With high sulfoxide/sulfone selectivities, the efficient conversion of **1a** into methyl phenyl sulfoxide **2a** was achieved with 1 mol % $Rh_2(esp)_2$ and 5 equiv of T-HYDRO as the oxidant in dichloromethane (DCM) under ambient conditions (Table 1, entry 1).[7f−k] In the absence of T-HYDRO, no conversion was observed (Table 1, entry 4). In the absence of catalyst, only 32% of **2a** was obtained after 6 h (Table 1, entry 3). Dioxygen did not play a role in the reaction (Table 1, entry 5). When the amount of T-HYDRO was reduced to 3 or 1 equiv, a significantly lower conversion was observed (Table 1, entries 6 and 7). Other oxidants such as cumene hydroperoxide and 30% aqueous hydrogen peroxide were also tested. However, the activity of the reaction decreased when cumene hydroperoxide was used and no conversion occurred when using 30% aqueous hydrogen peroxide (Table 1, entries 8 and 9). The catalytic reaction was found to be solvent dependent. Polar solvents such as acetonitrile and actetone were not suitable because they coordinate to dirhodium catalysts and block the axial reaction site.[9] Reactions performed in nonpolar solvents such as heptane

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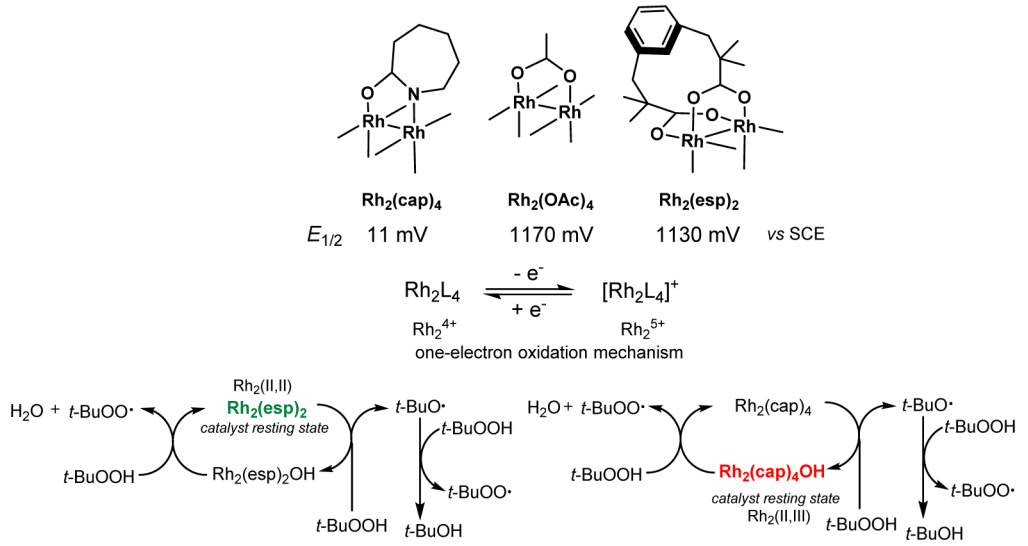


Figure 1. One-electron oxidative procedure of dirhodium(II) catalysts.

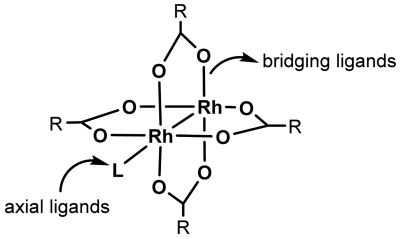
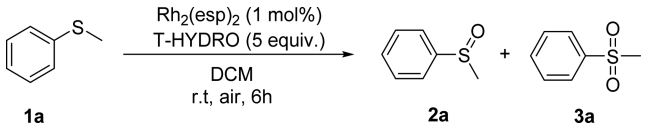


Figure 2. Structure of dirhodium(II) carboxylate catalysts.

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	deviation from standard reaction conditions	sulfoxide selectivity (%)[b]	2a yield (%)[c]
1	none	>99	96
2[d]	without solvent	>99	74
3	without $Rh_2(esp)_2$	>99	32
4	without T-HYDRO	–	NR
5	N_2 instead of air	>99	92
6	3 equiv of T-HYDRO	98	87
7	1 equiv of T-HYDRO	>99	33
8	30% H_2O_2 instead of T-HYDRO	–	–
9	cumene instead of T-HYDRO	99	84
10	acetonitrile instead of DCM	95	64
11	*n*-heptane instead of DCM	>99	80
12	acetone instead of DCM	97	74
13	0.1 mol % $Rh_2(esp)_2$	>99	52
14	$Rh_2(OAc)_4$ instead of $Rh_2(esp)_2$	>99	35
15	$Rh_2(OAc)_4$(IMes) instead of $Rh_2(esp)_2$	>99	71
16	$Rh_2(MPDP)_2$ instead of $Rh_2(esp)_2$	>99	39

[a]Reaction conditions: **1a** (0.9 mmol), $Rh_2(esp)_2$ (0.009 mmol), T-HYDRO (4.5 mmol), DCM (1.8 mL), rt, 6 h, air atmosphere, unless otherwise noted. [b]Determined by ^1H NMR; selectivity = **2a**(mol) /(**2a**(mol) + **3a**(mol)) × 100%. [c]Yield after column chromatography. [d]Reaction time: 8 h.

also gave less yield when compared to reactions run in DCM (Table 1, entries 10–12). It is important to note that a catalyst loading of 0.1 mol % $Rh_2(esp)_2$ could give 52% **2a** after 6 h (Table 1, entry 13). Other dirhodium(II) catalysts were also tested for this reaction. However, they were not as effective as $Rh_2(esp)_2$ (Table 1, entries 14–16). Interestingly, while $Rh_2(OAc)_4$ has a nearly identical potential for one-electron oxidation compared to $Rh_2(esp)_2$,[10] using $Rh_2(OAc)_4$ only gave a 35% yield. $Rh_2(OAc)_4$(IMes) was also tested but only gave 71% yield.[11] Low yields were obtained when carrying out the reaction with structurally similar chelating dirhodium(II) catalysts.[12]

After the optimized reaction conditions were determined, the substrate scope of the reaction was tested. A variety of organic sulfides **1b–o** were oxidized to their corresponding sulfoxides **2b–o** with excellent selectivities and yields (Table 2). Different substituted-phenyl groups in the methyl aryl sulfides **1b–g** are well-tolerated (Table 2, entries 1–6). However, sulfides bearing electron-withdrawing substituents required longer reaction times for high conversion (Table 2, entries 4–6). The ethyl substitution at sulfur did not slow down the reaction rate (Table 2, entry 7). This method proved tolerant of the tested functional groups such as alcohols and alkenes. For instance, sulfides with oxidation-susceptible functionalities (**1i–k**) gave sulfoxides **2i–k** without affecting the sensitive functional groups (Table 2, entries 8–10). The less reactive diphenyl sulfide **1l** and thianthrene **1m** were both oxidized in good yields (Table 2, entries 11 and 12). Alkyl sulfides **1n–o** were also oxidized to their corresponding sulfoxides **2n–o** in good yields and with excellent chemoselectivity (Table 2, entries 13 and 14).

During the reaction, many color changes occur. These color changes were studied to give us mechanistic information about the oxidation reaction. UV/vis spectroscopy was used to monitor the oxidation reaction of **1a** (Figure 3).[9] When $Rh_2(esp)_2$ was dissolved in DCM, a transparent green solution showed the characteristic band $Rh_2\pi^*$ to $Rh_2\sigma^*$ of $Rh_2(esp)_2$ at 661 nm.[4] Figure 3 shows that the band $Rh_2\pi^*$ to $Rh_2\sigma^*$ shifts 107 nm after substrate **1a** was added. Previous reports have shown that the energy of $Rh_2\pi^*$ to $Rh_2\sigma^*$ HOMO to LUMO transition is strongly affected by axially coordinated ligands.[11,13] This large shift indicates that **1a** strongly binds to rhodium. Upon adding one portion of T-HYDRO, the UV/vis spectrum remained relatively unchanged and there was no band that corresponded to typical one-electron oxidized Rh_2(II,III) species (about 800 nm). This suggests that Rh_2(II,II) is the catalyst resting state.

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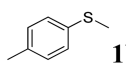
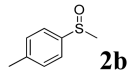
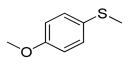
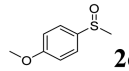
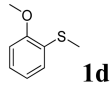
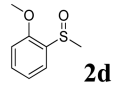
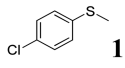
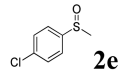
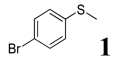
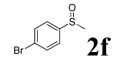
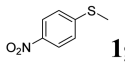
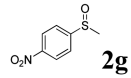
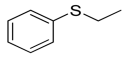
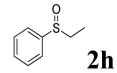
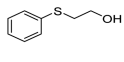
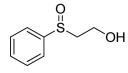
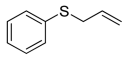
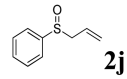
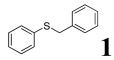
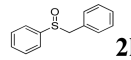
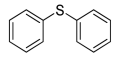
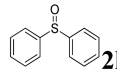
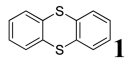
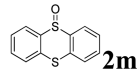
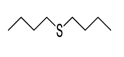
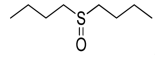
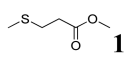
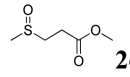
Table 2. Oxidation of Various Sulfides with T-HYDRO Catalyzed by $Rh_2(esp)_2$[a]

Entry	Substrate	Product	Time(h)	Selectivity(%)[b]	Yield(%)[c]
1	 1b	 2b	4	>99	97
2	 1c	 2c	5	>99	96
3	 1d	 2d	2	98	96
4	 1e	 2e	11	99	98
5	 1f	 2f	34	>99	87
6	 1g	 2g	59	99	88
7	 1h	 2h	5	>99	99
8	 1i	 2i	10	91	81
9	 1j	 2j	6	92	89
10	 1k	 2k	8	85	84
11	 1l	 2l	12	98	97
12	 1m	 2m	13	96	99
13[d]	 1n	 2n	6	>99	89
14[e]	 1o	 2o	8	99	70

[a]Reaction conditions: sulfides **1** (0.9 mmol), $Rh_2(esp)_2$ (0.009 mmol), T-HYDRO (4.5 mmol), DCM (1.8 mL), rt, air atmosphere, unless otherwise noted. [b]Determined by ^1H NMR; selectivity = **2**(mol)/(**2**(mol) + **3**(mol)) × 100%. [c]Yield after column chromatography. [d]1.5 eq. of T-HYDRO. [e]3 equiv of T-HYDRO.

Over the course of the reaction, the color gradually became red which implies that the product sulfoxide **2a** becomes coordinated to the dirhodium(II) compound as the concentration of substrate **1a** decreases. At the end of the reaction, the band $Rh_2\pi^*$ to $Rh_2\sigma^*$ was shifted to 506 nm.

After the reaction was completion and workup, the $Rh_2(esp)_2$–sulfoxide complexes directly precipitated and were recovered by simple filtration. The structure of the precipitated $Rh_2(esp)_2$–bis-sulfoxide complex **2c** was confirmed by X-ray crystallography (see Supporting Information (SI)). Actually, it was reported in the solution that one of the two axial ligands could be displaced and leave one vacant axial coordination site on the dirhodium(II) complexes.[9c,d,13]

In other $Rh_2(esp)_2$-catalyzed reactions such as intermolecular amination, DCM is not a suitable solvent, as it is oxidized (likely through C–H abstraction) under the strong oxidation conditions.[4,14] The Cl^- can then axially coordinate to one-electron oxidized $Rh_2(esp)_2^+$ to result in the $Rh_2(esp)_2Cl$ adduct which is inactive for catalysis (Scheme 1).

Interestingly, even though we also observed the formation of $Rh_2(esp)_2Cl$ in DCM upon addition of T-HYDRO, the

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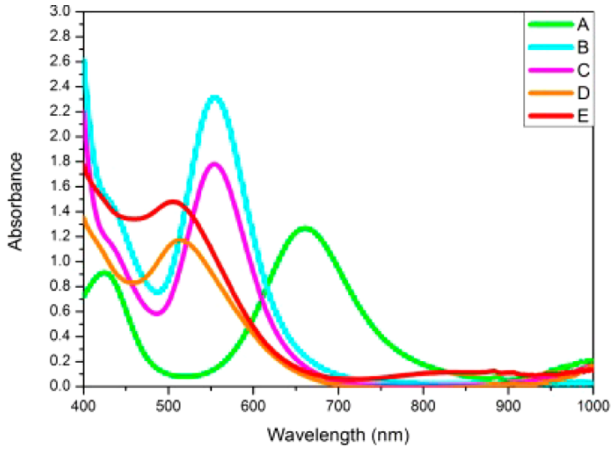
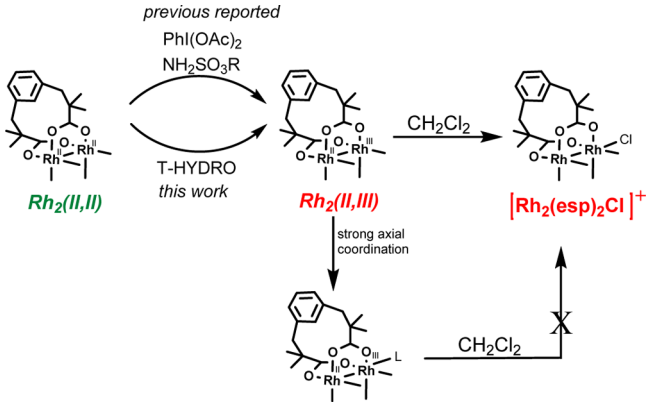


Figure 3. (A) $Rh_2(esp)_2$ in CH_2Cl_2 (λ_{max} = 661 nm). (B) $Rh_2(esp)_2$ and **1a** in CH_2Cl_2 (λ_{max} = 554 nm). (C) $Rh_2(esp)_2$, **1a** and T-HYDRO in CH_2Cl_2 (1 h, λ_{max} = 554 nm). (D) $Rh_2(esp)_2$, **1a** and T-HYDRO in CH_2Cl_2 (3 h, λ_{max} = 514 nm). (E) $Rh_2(esp)_2$, **1a** and T-HYDRO in CH_2Cl_2 (6 h, λ_{max} = 506 nm).

Scheme 1. Formation of $Rh_2(esp)_2Cl$



catalysis continued once sulfide was added (Figure 4, II). We propose that $Rh_2(esp)_2Cl$ does not exist in the presence of sulfide because sulfides are strong ligands that occupy the axial sites of the dirhodium(II) catalyst, avoiding generated $Rh_2(esp)_2^+$ to react with DCM (Scheme 1). Because sulfoxides have been shown to be ambidentate ligands,[15] we tested our hypothesis by subjecting methyl 2-methoxyphenyl sulfide **1d** to our oxidation conditions (Figure 4, I). Unlike other oxidation cases, we observed the reaction mixture change from a purple red color to green over the course of the 2 h reaction and the $Rh_2\pi^*$ to $Rh_2\sigma^*$ band shifted back to around 620 nm. X-ray crystal analysis helped discern these changes (see SI $Rh_2(esp)_2$–bis-**2d**: its formation and isolation are the same as $Rh_2(esp)_2$–bis-**2c**). It is important to note that $Rh_2(esp)_2$ coordinates to sulfoxide **2d** through the oxygen atom and not the sulfur atom. It is also interesting that the green color slowly turned to red after 10 min and a band at 847 nm could be observed in the UV/vis spectra; this is typical for a one-electron oxidized Rh_2(II,III) species.[4] This band was similar to the band observed in the absence of substrate (Figure 4, III). This suggests that the $Rh_2(esp)_2Cl$ adduct was formed. Sulfoxide **2d** coordinates to the metal center through the weak electron donor oxygen atom which is not able to prevent DCM oxidation.

Another factor besides ligand coordination ability (i.e., redox potential) could also explain why DCM oxidation does not occur in this catalytic reaction. It has been reported that axial ligands coordinating to a dirhodium(II) center can change the redox potential of the complex.[13] Therefore, cyclic voltammetry (CV) experiments were performed to measure the redox potentials over the course of the reaction (Figure 5). Interestingly,

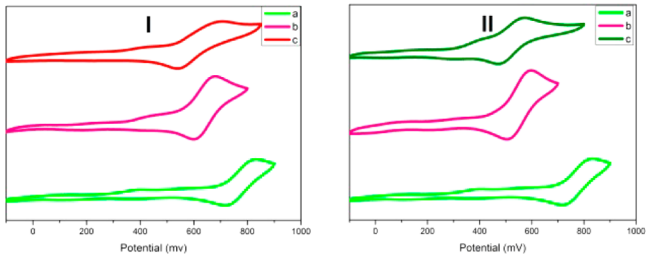


Figure 5. I (a) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) ($E_{1/2}$ = 781 mV). (b) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) + **1a** (20 equiv) ($E_{1/2}$ = 642 mV). (c) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) + **2c** (20 equiv) ($E_{1/2}$ = 623 mV). II (a) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) ($E_{1/2}$ = 781 mV). (b) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) + **1d** (20 equiv) ($E_{1/2}$ = 553 mV). (c) $Rh_2(esp)_2$ (5.0×10^{-4} mol L^{-1} in CH_2Cl_2 solution) + **2d** (20 equiv) ($E_{1/2}$ = 523 mV).

the Rh_2(II,II)/Rh_2(II,III) has a redox couple that is 139 mV more accessible than that for $Rh_2(esp)_2$ when **1a** was added. The redox potential of $Rh_2(esp)_2$-**2d** ($E_{1/2}$ = 523 mV vs Fc/Fc^+) was lower

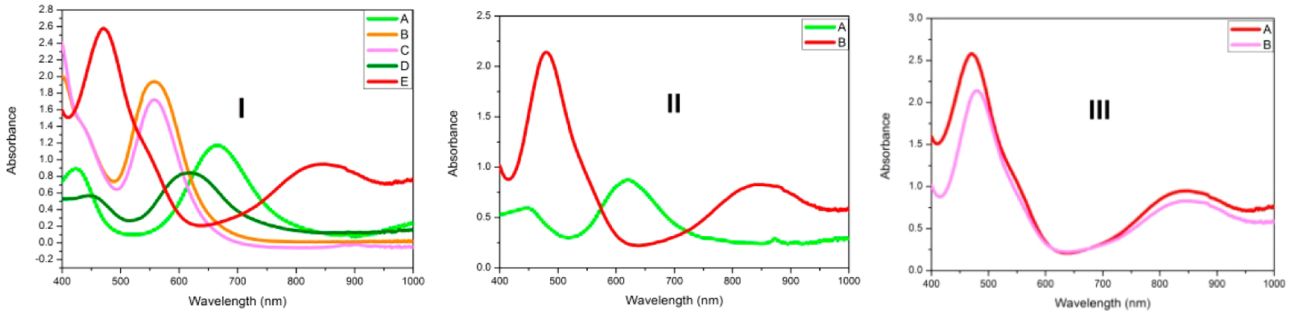


Figure 4. I (A) $Rh_2(esp)_2$ in CH_2Cl_2 (λ_{max} = 666 nm). (B) $Rh_2(esp)_2$ and **1d** in CH_2Cl_2 (λ_{max} = 557 nm). (C) $Rh_2(esp)_2$, **1d**, and T-HYDRO in CH_2Cl_2 (1 h, λ_{max} = 557 nm). (D) The oxidation reaction mixture of **1d** when the reaction finished (λ_{max} = 620 nm). (E) The oxidation reaction mixture of **1d** stood for 10 min after the reaction was finished (λ_{max} = 847 nm). II (A) $Rh_2(esp)_2$ and T-HYDRO in Benzene (λ_{max} = 620 nm). (B) $Rh_2(esp)_2$ and T-HYDRO in DCM (λ_{max} = 848 nm). III (A) The oxidation reaction mixture of **1d** stood for 10 min after the reaction was finished (λ_{max} = 847 nm). (B) $Rh_2(esp)_2$ and T-HYDRO in DCM (λ_{max} = 848 nm).

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than that of the redox potential of $Rh_2(esp)_2$-**2c** ($E_{1/2}$ = 623 mV vs Fc/Fc^+). This lower redox potential further explains why the $Rh_2(esp)_2Cl$ adduct can form when **2d** is an axial ligand. This experiment also shows that the axial ligand at the Rh center can fine-tune the redox potentials of the dirhodium(II,II) compounds and affect the predominant catalyst species during the reaction.

After establishing the high stability of $Rh_2(esp)_2$ during the reaction, we investigated the recyclability and reusability of the catalyst using **1a** as a model substrate. At the end of the reaction and workup, the $Rh_2(esp)_2$ catalyst in $Rh_2(esp)_2$–bis-**2a** complex form was recovered by filtration, washed with cold ethyl acetate, and dried. It was then directly reused in a subsequent experiment with fresh **1a** and oxidant under similar reaction conditions. Four recycling experiments were carried out, and the results are summarized in Table 3. The catalyst

Table 3. Catalyst Recycling Experiments[a]

cycle	$Rh_2(esp)_2$ recovery yield (%)	product yield (%)
1	94	91
2	87	90
3	88	99
4	87	98

[a]Reaction condition: $Rh_2(esp)_2$ (1 mmol %), **1a**, T-HYDRO, CH_2Cl_2, rt, 6 h, air.

recovery rate and product yield remained relatively constant, which confirms the robustness of this oxidation protocol. Another recycling experiment was performed by using a batch of $Rh_2(esp)_2$ catalyst to successively catalyze six different sulfide oxidation reactions (Scheme 2). After each reaction, the $Rh_2(esp)_2$–sulfoxide complexes were collected and used directly to catalyze the next reaction. It is noteworthy that there was no obvious decrease in sulfoxide yield when using the recovered catalyst compared to a new batch of catalyst. At the end of the recycling experiment, the $Rh_2(esp)_2$–sulfoxide complex was passed through a column to obtain pure $Rh_2(esp)_2$ catalyst.

On the basis of the above results and the literature available involving sulfoxidation, a possible catalytic cycle has been proposed that involves a single electron transfer (SET).[16] First, a one-electron transfer from sulfenyl sulfur to *tert*-butylperoxy radical (*t*-BuOO•) generated by $Rh_2(esp)_2$ occurs to give the corresponding sulfenium radical (Scheme 3).[16] The resultant sulfenium radical then undergoes fast chemical transformation with *tert*-butylperoxy radical to afford the corresponding sulfoxide. The one-electron oxidation to dirhodium(II,III) is the rate-limiting step which means that the catalyst resting state is the stable dirhodium(II,II) complex. This helps avoid oxidative degradation and catalyst deactivation which allows for the $Rh_2(esp)_2$ catalyst to be recovered and reused again. The details of how $Rh_2(esp)_2$ controls the oxidation state of the catalyst resting state during the reaction and how the chelating ligand affects the reaction remain to be investigated.

CONCLUSION

A simple, efficient, and environmentally friendly method for the oxidation of sulfides to sulfoxides using $Rh_2(esp)_2$ as catalyst and safe aqueous T-HYDRO as oxidant has been developed. Because of the unique structure of the dirhodium(II) compound, catalyst/product separation is very simple. It was demonstrated that $Rh_2(esp)_2$ could be reused without considerable loss of activity due to a stable $Rh_2(II,II)$ catalyst resting state during the oxidation reaction. Further experiments will be performed to elucidate the mechanism in detail and to broaden the scope of the reaction.

EXPERIMENTAL SECTION

General. All reagents were purchased unless otherwise noted. Reactions were run under atmospheric conditions at room temperature. CH_2Cl_2 was distilled from CaH_2. Ethyl acetate, *n*-hexane, and diethyl ether were purchased from commercial sources and used without further purification. $Rh_2(esp)_2$ was prepared according to the literature.[17,18] $Rh_2(MPDP)_2$ and $Rh_2(OAc)_4(IMes)$ preparations have been previously reported.[19,20]

For the ^1H, ^{13}C NMR spectra (^1H NMR 300, 400 MHz, ^{13}C NMR 75, 100 MHz), $CDCl_3$ was used as the solvent. Chemical shifts are reported in δ (ppm) relative to TMS (δ = 0.00 ppm). Electrochemical measurements were performed in anhydrous CH_2Cl_2 with tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The electrochemical measurements system was constructed using a Pt disk working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ (0.1 mol L^{-1} in acetonitrile) reference electrode. For cyclic voltammetry, data were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc^+). Melting points were uncorrected. The high-resolution mass spectra (HRMS) were performed on a mass spectrometer with a TOF (for ESI).

Typical Sulfide Oxidation Procedure. The oxidation reaction was carried out in a 10 mL tube containing a magnetic stirrer. CH_2Cl_2 (1.8 mL) and methyl phenyl sulfide **1a** (112.0 mg, 0.9 mmol) were added into the reactor charged with $Rh_2(esp)_2$ (6.8 mg, 0.009 mmol) under stirring and then sealed by a rubber plug with a needle. T-HYDRO (0.64 mL, 4.5 mmol) was then added via syringe. After the reaction was complete, the reaction mixture was quenched by the addition of 10 mL of saturated sodium thiosulfate solution and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried by anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product. The crude product was analyzed by ^1H NMR to obtain the selectivity of the oxidation reaction. The crude product was purified by silica gel flash chromatography (*n*-hexane/EtOAc = 5/1, then 1/3) to give methyl phenyl sulfoxide (**2a**)[7f] (119 mg, 96%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.55–7.46 (m, 3H), 2.71 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.6, 131.0, 129.3, 123.4, 43.9. HRMS (ESI-TOF): *m*/*z* calculated for C_7H_8OS ($[M + H]^+$) 141.0369, found 141.0346.

*Methyl 4-methylphenyl sulfoxide (**2b**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/3) afforded 133 mg (97%); yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.67 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.3, 141.3, 129.9, 123.8, 43.9, 21.2.

*4-Methoxyphenyl methyl sulfoxide (**2c**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 145 mg (96%); yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 2.63 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 161.7, 136.8, 125.4, 114.5, 55.3, 43.6. HRMS (ESI-TOF): *m*/*z* calculated for $C_8H_{10}O_2S$ ($[M + H]^+$) 171.0474, found 171.0442.

*2-Methoxyphenyl methyl sulfoxide (**2d**):*[7k] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 145 mg (96%); yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.46–7.38 (m, 1H), 7.18–7.13 (m, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 2.74 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 154.6, 132.9, 131.8, 124.4, 121.5, 110.5, 55.5, 41.1. HRMS (ESI-TOF): *m*/*z* calculated for $C_8H_{10}O_2S$ ($[M + H]^+$)171.0474, found 171.0451.

*4-Chlorophenyl methyl sulfoxide (**2e**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/3) afforded 151 mg (98%); yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 2.70 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.2, 137.2, 129.6, 124.9, 44.0.

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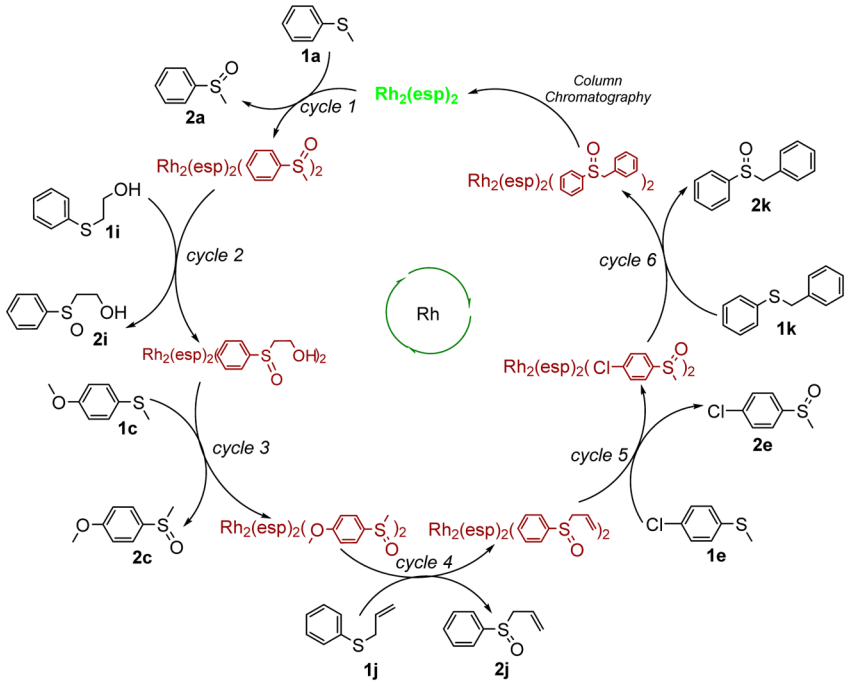
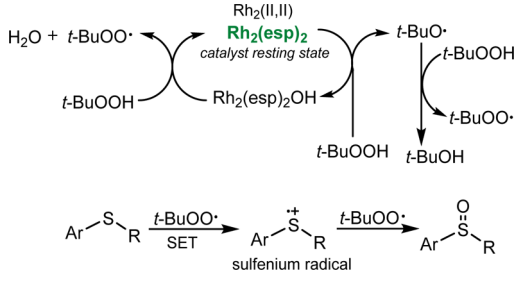
Scheme 2. Catalyst Recycling Experiments



Cycle	Time/h	$Rh_2(esp)_2$ recovery yield (%)	Product yield(%)
1	4	88	98
2	9	99	97
3	4	90	99
4	6	95	99
5	11	94	89
6	8	83	92

Scheme 3. Possible Mechanism



HRMS (ESI-TOF): m/z calculated for C_7H_7ClOS ([M + H]$^+$)-174.9979, found 174.9945.

*4-Bromophenyl methyl sulfoxide (**2f**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 168 mg (87%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 2.69 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 132.6, 125.5, 125.2, 44.0.

*4-Nitrophenyl methyl sulfoxide (**2g**):*[7i] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 144 mg (88%); white solid, mp 153−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.9 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H), 2.78 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 149.5, 124.7, 124.5, 43.9. HRMS (ESI-TOF): m/z calculated for $C_7H_7NO_3S$ ([M + H]$^+$) 186.0219, found 186.0236.

*Phenyl ethyl sulfoxide (**2h**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/3) afforded 135 mg (99%); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.54 (m, 2H), 7.53−7.43 (m, 3H), 2.88 (m, 1H), 2.80−2.67 (m, 1H), 1.17 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 143.1, 130.8, 129.0, 124.0, 50.1, 5.8.

*2-(Phenylsulfinyl)ethanol (**2i**):*[7g] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 122 mg (81%); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.56 (m, 2H), 7.54−7.42 (m, 3H), 4.32 (s, 1H), 4.15−4.09 (m, 1H), 3.97−3.85 (m, 1H), 3.11−3.03 (m, 1H), 2.94−2.87 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 143.0, 131.1, 129.3, 123.9, 59.6, 56.0. HRMS (ESI-TOF): m/z calculated for $C_8H_{10}O_2S$ ([M + H]$^+$) 171.0474, found 171.0421.

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*Allyl phenyl sulfoxide (**2j**):*[7g] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/3) afforded 131 mg (89%); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.44 (m, 5H), 5.71−5.57 (m, 1H), 5.36−5.14 (m, 2H), 3.60−3.46 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.8, 131.0, 128.9, 125.1, 124.2, 123.7, 60.7.

*Benzyl phenyl sulfoxide (**2k**):*[7h] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1) afforded 160 mg (84%); white solid, mp 127−128 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.32 (m, 5H), 7.32−7.19 (m, 3H), 7.01−6.93 (m, 2H), 4.08 (d, J = 12.6 Hz, 1H), 3.99 (d, J = 12.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.7, 131.1, 130.3, 129.1, 128.8, 128.4, 128.2, 124.4, 63.5.

*Diphenyl sulfoxide (**2l**):*[7f] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/1) afforded 174 mg (97%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.64 (m, 4H), 7.52−7.43 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.6, 131.1, 129.4, 124.8.

*Thianthrene 5-oxide (**2m**):*[7j] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1) afforded 203 mg (99%); white solid, mp 146−148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94−7.91 (m, 2H), 7.63−7..61 (m, 2H), 7.57−7.52 (m, 2H), 7.45−7.39 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 141.3, 129.8,129.7, 128.9, 128.3, 124.3.

*Dibutyl sulfoxide (**2n**):*[7g] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then 1/1) afforded 128 mg (89%); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69−2.52 (m, 4H), 1.75−1.63 (m, 4H), 1.55−1.33 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 52.0, 24.4, 21.9, 13.5.

*Methyl 3-(methylsulfinyl)propanoate (**2o**):*[7i] Typical procedure was followed and flash chromatography (silica gel, *n*-hexane/EtOAc = 5/1, then EtOAc) afforded 93 mg (70%); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.07−2.96 (m, 1H), 2.90−2.74 (m, 3H), 2.55 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 171.4, 52.0, 48.7, 38.6, 26.5. HRMS (ESI-TOF): m/z calculated for $C_5H_{10}O_3S$ ($[M + H]^+$) 151.0423, found 151.0421.

Procedure for Precipitating the $Rh_2(esp)_2$−Bis-sulfoxide Complexes and Catalyst Recycling Experiment. The oxidation reaction was performed in a round-bottomed flask containing a magnetic stirrer at room temperature. DCM and sulfide **1** were added into a reactor charged with $Rh_2(esp)_2$ under stirring. The reactor was then sealed by a rubber plug with a needle. T-HYDRO was subsequent added via syringe. After completion of the reaction, saturated sodium thiosulfate solution was added to the mixture to quench the reaction. The mixture was then extracted with ethyl acetate. The organic layer was separated and dried over anhydrous Na_2SO_4. After evaporation of the solvent, precipitating agents were added to precipitate the $Rh_2(esp)_2$−bis-sulfoxide complexes. The red catalysts complexes were separated by filtration. The product sulfoxides were obtained after the solvents were removed under reduced pressure. The obtained catalysts complexes were washed with cold ethyl acetate and then dried in air with high recovery yield (based on the $Rh_2(esp)_2$), which would be directly used as catalysts in the next cycle. Pure $Rh_2(esp)_2$ would be recovered by decomplexing the $Rh_2(esp)_2$−bis-sulfoxides through a silica gel column using *n*-hexane/ethyl acetate as elution solvents.

*$Rh_2(esp)_2$−bis-**2a**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77−7.75 (m, 4H), 7.51−7.45 (m, 6H), 7.10−7.08 (m, 2H), 6.83 (s, 2H), 6.83−6.81 (m, 4H), 2.97 (s, 6H), 2.55 (s, 8H), 0.92 (s, 24H). Cocrystallized solvent molecules were not counted.

*$Rh_2(esp)_2$−bis-**2c**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 4H), 7.09 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 8.4 Hz, 4H), 6.87 (s, 2H), 6.84−6.82 (m, 4H), 3.87 (s, 6H), 3.04 (s, 6H), 2.58 (s, 8H), 0.93 (s, 24H).

*$Rh_2(esp)_2$−bis-**2e**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.5 Hz, 4H), 7.11 (t, J = 7.8 Hz, 2H), 6.85 (s, 2H), 6.85−6.83 (m, 4H), 3.05 (s, 6H), 2.57 (s, 8H), 0.92 (s, 24H).

*$Rh_2(esp)_2$−bis-**2i**.* ^{1}H NMR (400 MHz, CDCl3) δ 7.75−7.73 (m, 4H), 7.54−7.48 (m, 6H), 7.09 (t, J = 7.5 Hz, 2H), 6.82−6.79 (m, 4H), 6.79 (s, 2H), 4.26−4.12 (m, 4H), 3.28−3.18 (m, 4H), 2.55 (s, 8H), 0.91 (s, 24H). Cocrystallized solvent molecules were not counted.

*$Rh_2(esp)_2$−bis-**2j**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−769 (m, 4H), 7.52−7.43 (m, 6H), 7.08 (t, J = 7.5 Hz, 2H), 6.85 (s, 2H), 6.85−6.81 (m, 4H), 5.79−5.67 (m, 2H), 5.35−5.32 (m, 2H), 5.20−5.15 (m, 2H), 4.08−4.03 (m, 2H), 3.88−3.79 (m, 2H), 2.57 (s, 8H), 0.93 (s, 24H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02400.

Pictures of solution color of the sulfide oxidation reaction, complete recycling experiments, and copies of ^{1}H and ^{13}C spectra for all products (PDF)

Crystallographic data for $Rh_2(esp)_2$−bis-**2c** (CIF)

Crystallographic data for $Rh_2(esp)_2$−bis-**2d** (CIF)

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Notes

The authors declare no competing financial interest.

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