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Diruthenium(II,III) Bis(tetramethyl-1,3-benzenedipropionate) as a Novel Catalyst for *tert*-Butyl Hydroperoxide Oxygenation

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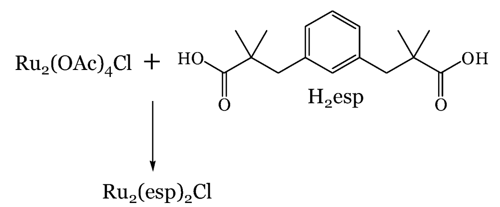
The reaction of $Ru_2(OAc)_4Cl$ with 2.2 equiv of H_2esp (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate) resulted in a new compound, $Ru_2(esp)_2Cl$ (**1**), that is soluble in organic media. **1** is an active catalyst for the oxygenation of organic sulfides by *tert*-butyl hydroperoxide (TBHP) in both an acetonitrile solution or neat (solvent-free) conditions. Solvent-free reactions display the quantitative utility of TBHP and hence excellent chemical selectivity for sulfoxide formation.

Scheme 1. Preparation of **1**[a]



[a] Conditions: $Ru_2(OAc)_4Cl$, 2.2 equiv of H_2esp, H_2O/CH_3OH (v/v, 1:2); 3 h of reflux.

The catalyzed oxygenation of organic sulfides is an important transformation for medicinal chemistry,[1] petroleum desulfuridization,[2] and nerve agent detoxification.[3] For the last two applications, the reaction rates, nature of both the oxidants and catalysts, and the chemical selectivity between sulfoxide and sulfone products are highly relevant issues. Hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP) are among the desired oxidants because of both their low costs and environmentally friendly nature.[4] Hydrogen peroxide is the most studied[5] and can be activated with a variety of transition-metal-based homogeneous catalysts. In comparison, *tert*-butyl hydroperoxide is difficult to activate and is less studied.[6] The earliest example of catalytic oxidation by TBHP was reported by Kuhnen,[7] in which thioanisole was converted to methyl phenyl sulfone quantitatively in the presence of molybdenyl acetylacetonate. Recently reported efficient catalysts for TBHP include $MeReO(mtp)PPh_3$ [mtp = 2-(mercaptomethyl)thiophenol)] by Espenson et al.[8] and $(Me_3TACN)MnX_3$ (Me_3ATCN = 1,4,7-*N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane and X = Cl^- and Br^-) by us.[9] In both cases, the optimal turnover frequencies (TOFs) are about 200 h^{-1}. Although efficient, both the Re and Mn catalysts invoked elaborately designed ligands and are hence expensive.

The feasibility of using dimetallic paddlewheel species to activate TBHP has been demonstrated in allylic and benzylic oxidation by TBHP in the presence of dirhodium(II) caprolactamate $[Rh_2(cap)_4]$ by Doyle and co-workers,[10,11] although Rh is also quite expensive. Encouraged by Doyle et al.'s success, we have been exploring the use of diruthenium species as the TBHP activators[12] and reported herein are the development of a novel compound $Ru_2(esp)_2Cl$ (**1**; Scheme 1) and the preliminary assessment of its capacity in promoting sulfide oxygenation by TBHP.

1 was prepared in excellent yield (88%) by refluxing $Ru_2(OAc)_4Cl$ with 2.2 equiv of H_2esp (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate)[13] in H_2O/CH_3OH (1:2).[14] Although **1** cannot be characterized by NMR because

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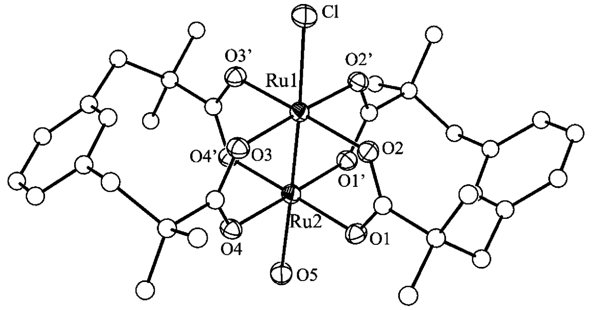

Figure 1. Structural plot of **1**. H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 2.2768(6); Ru1−Cl1, 2.4852(14); Ru1−O1, 2.034(2); Ru1−O3, 2.028(2); Ru2−O2, 2.021(2); Ru2−O4, 2.009(2); Ru2−O5, 2.342(3); Ru2−Ru1−Cl1, 177.64(4); Ru1−Ru2−O5, 178.81(9); Ru−Ru′−O(av), 89.43(7). There is a crystallographic mirror that contains the Ru2−Ru1−Cl vector and bisects both esp ligands.

of its paramagnetic nature ($S = {}^{3}/_{2}$), its identity has been confirmed by both fast atom bombardment mass spectrometry (FAB-MS) and combustion analyses. Its molecular structure was determined through a single-crystal X-ray diffraction study,[15] and the structural plot is shown in Figure 1. It is clear from Figure 1 that the esp ligand coordinates to the Ru_2 core as a tetradentate chelate, and the overall geometric feature of the paddlewheel core is very similar to those of $Rh_2(esp)_2$[13] and $Re_2(esp)_2Cl_2$.[16] One of the two axial positions is occupied by the chloro ligand, a feature common to all $Ru_2(O_2CR)_4Cl$-type compounds,[17] while the other is occupied by a water molecule. The same axial ligation pattern was observed for $Ru_2(O_2CCMe_3)_4Cl$.[18] The Ru−Ru distance in **1** [2.2768(6) Å] is identical with that in $Ru_2(O_2CCMe_3)_4Cl$ [2.274(2) Å] within the experimental error, and both are within the range of the Ru−Ru distance in $Ru_2(O_2CR)_4X$-type compounds, 2.248–2.292 Å.[19]

Successful preparation of **1** was followed by the examination of its activity in facilitating TBHP oxygenation of organic sulfides. Organic sulfides studied were methyl phenyl sulfide (MPS), diphenyl sulfide (PPS), ethyl phenyl sulfide (EPS), and 2-chloroethyl phenyl sulfide (CEPS), which are shown in Scheme 2 along with the oxygenation reaction of these sulfides. Initial catalytic reactions were performed with MPS in CH_3CN, and the data obtained through gas chromatography−mass spectrometry (GC−MS) analysis are given in Table 1. As shown in entries 1–4, **1** is active for the oxygenation of MPS. Furthermore, the formation of methyl phenyl sulfoxide was dominant even with TBHP in significant excess. With the catalyst loading at 1 mol %, MPS was consumed in 24 h to yield the corresponding sulfoxide (70%) and sulfone (30%), which correspond to a TOF of 5 h^{-1}.

Scheme 2. Oxygenation of Organic Sulfides

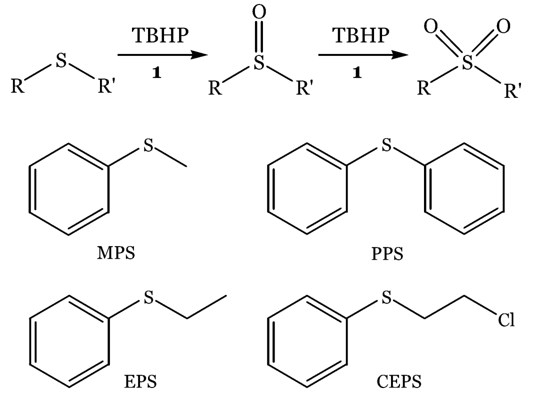

Table 1. Catalytic Oxygenation of Organic Sulfides

entry	RSR′	t/h	RSR′ %	RS(O) R′ %	RS(O)$_2$ R′ %	“other”	TOF^a/h^{-1}
1	MPS	1	82	15	3	0	20
2		4	43	52	5	0	16
3		12	2	85	13	0	9
4		24	<1	70	29	0	5
5	PPS	12	8	82	10	0	8.5
6		24	7	74	19	0	5
7	EPS	2	96	1	2	1^b	1.5
8		48	9	45	20	26^b	
9	CEPS	4	84	$4^c + 3^d$		9^e	2
10		48	29	$11^c + 24^d$	2	$24^e + 10^b$	

In all reactions, 1.25 mmol of sulfide, 1 mol % of **1**, and 8 equiv of TBHP were mixed in 5 mL of CH_3CN at 21 (±2) °C; an aliquot of the reaction was analyzed by GC−MS at the specified time. [a] Turnover frequency (h^{-1}) = {[RR′SO] + 2[RR′SO$_2$]}/{[Cat] × time (h)}. [b] Phenyl disulfide and corresponding sulfoxide. [c] Phenyl vinyl sulfoxide. [d] Chloroethyl phenyl sulfoxide. [e] EPS.

With the success of MPS oxygenation, catalyzed oxygenations of PPS, EPS, and CEPS were subsequently examined using the same level of catalyst loading, and the results are also collected in Table 1. The reactivity of PPS is comparable to that of MPS in terms of both the rate (TOF) and distribution of products. In contrast, oxygenation of both CEPS and EPS was slow and resulted in large amounts of byproducts, similar to our previous studies of oxygenation by both H_2O_2 and TBHP.[9,20] The formation of elimination products such as phenyl vinyl sulfoxide from CEPS is attributed to the formation of a sulfenium intermediate via a single-electron-transfer (SET) mechanism, as noted in our prior discussion.[9]

The efficacy of **1** in activating TBHP for sulfide oxygenation encouraged further study of the system’s reaction

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(14) $Ru_2(OAc)_4Cl$ (200 mg, 0.422 mmol) and H_2esp ligands (259 mg, 0.929 mmol) were refluxed in a mixture of H_2O (20 mL) and MeOH (30 mL) for 3 h. Upon the removal of most of MeOH, the precipitate formed was collected by filtration and rinsed with water. The crude product was purified on a short silica gel column with EtOAc/hexanes (3:1) to yield a golden burgundy solid (294 mg, 88.0% based on ruthenium). For the purpose of analysis, the product was recrystallized from CH_2Cl_2 and dried under vacuum for 2 days. FAB-MS (*m/e*, based on ^{101}Ru): 756 [$M^+ - Cl$]. Anal. for $Ru_2(esp)_2Cl\cdot 0.5CH_2Cl_2$. Found (calcd): C, 46.60 (46.65); H, 5.37 (5.42).

(15) X-ray diffraction data for crystal **1** were collected on a Bruker SMART1000 CCD diffractometer using Mo Kα at 300 K. Crystal data for $Ru_2(esp)_2Cl\cdot 2CH_2Cl_2$: $C_{34}H_{44}Cl_5O_9Ru_2$, fw = 976.08, orthorhombic, *Pnma*, $a = 16.9347(7)$ Å, $b = 21.662(1)$ Å, $c = 11.2152(5)$ Å, $V = 4114.3(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.576$ g cm^{-3}. Of 20 916 reflections measured, 3729 were unique ($R_{int} = 0.064$). Least-squares refinement based on 3729 reflections with $I \geq 2\sigma(I)$ and 238 parameters led to convergence with final R1 = 0.037 and wR2 = 0.082.

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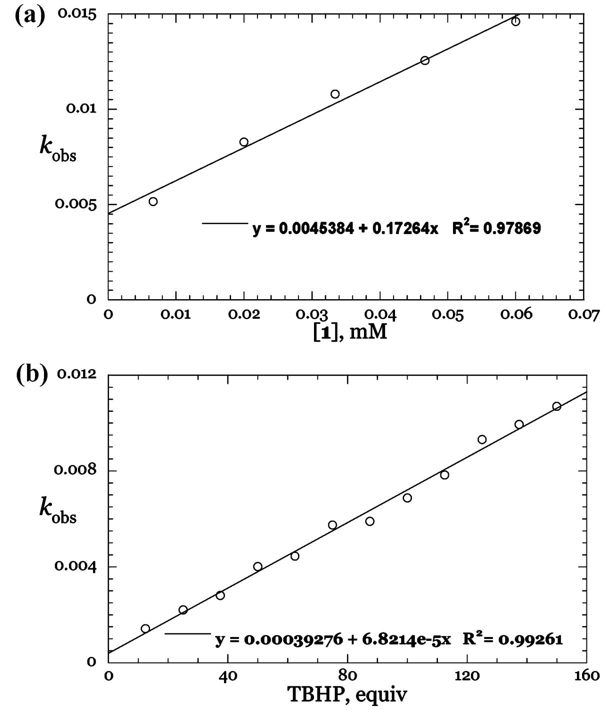

Figure 2. (a, top) Plots of k_{obs} from the variation of **1** in CH_3CN in the oxygenation of MPS with TBHP. (b) Plots of k_{obs} from the variation of TBHP in CH_3CN in the oxygenation of MPS with **1**.

kinetics, and a preliminary examination was based on the initial rates determined by monitoring of the disappearance of MPS at 290 nm, which has been used in analysis of MPS oxygenation in the work of Espenson and Pecoraro.[21,22] Two separate sets of experiments were performed. In the first, the effect of the concentration of the catalyst was analyzed by varying [**1**] in the presence of 2 mM MPS and 0.2 M TBHP, and the resultant $k_{obs}(1)$ vs [**1**] plot is shown in Figure 2a. It is clear from Figure 2a that the oxygenation reaction is first-order in **1**, which may indicate a single diruthenium compound as the active species. The nonzero intercept (ca. 0.004 min^{-1}) in Figure 2a is the rate of noncatalytic oxygenation, and its magnitude is consistent with those reported by Bateman and Hargrave.[23] In the second, the effect of the oxidant was studied in a CH_3CN solution that was 2 mM in both MPS and **1** through variation of [TBHP] (10–150 equiv). The resultant $k_{obs}(2)$ vs [TBHP] plot (Figure 2b) is also linear.

1 is soluble in organic media, which may enable catalytic oxygenations without the use of solvents because one or both reactants may function as the “solvent”. This aspect was carefully examined with MPS as the substrate, in which **1** is soluble. The reactions were highly exothermic upon initiation by the addition of TBHP and were kept at 0 °C for the first 15 min. Reaction mixtures were stirred vigorously because they were initially biphasic but coalesced with significant buildup of sulfoxide. As shown by entries in Table 2, the solvent-free reactions proceed much faster than those in CH_3CN, with the highest TOF around 2000 h^{-1} (entry 4). A comparison of entries 4 and 5 reveals that oxygenation of MPS is also more selective toward sulfoxide compared with the reactions in CH_3CN. Although 99% sulfoxide was produced within 1 h (entry 4), the highly concentrated mixture only produced 7% of sulfone in 24 h in the presence of excess TBHP (entry 5), demonstrating the selectivity of this catalyst for methyl phenyl sulfoxide formation. In addition, the *utility* of TBHP was nearly quantitative (entries 1 and 3). The much enhanced rates are clearly the result of increased effective concentrations of the reactants when combined in neat reagents.

Table 2. Solvent-Free Oxygenation Reactions with **1** and 8 mmol of MPS[a]

entry	**1**, mol %	TBHP equiv	*t*/h	MeSPh %	MeS(O) Ph %	$MeS(O)_2$ Ph %	TOF/h^{-1}
1	0.1	1	4	2	98	0	245
2	0.05	1	4	13	87	0	435
3			8	2	98	0	250
4	0.05	2	1	0	>99	<1	2000
5			24	0	93	7	

[a] Average of two runs.

Oxygenation of organic sulfides could take place through either a concerted direct oxo-transfer (two-electron-transfer) pathway or an initial SET to yield sulfenium and a subsequent oxygen-rebound pathway.[24] Direct oxo transfer has been the predominant mechanism of sulfide oxygenation by TBHP and probably accounts for most of the reactivity observed in this work. Nevertheless, the detection of phenyl vinyl sulfoxide during oxygenation of CEPS is a clear indicator of the involvement of the SET pathway.[9] The interaction and/or binding mode of TBHP to the diruthenium catalyst is another interesting but unresolved issue. Doyle and co-workers speculated that $Rh_2(cap)_4$ activates *tert*-butyl hydroperoxide by binding $^tBuOO^-$ at one of the axial positions with the concurrent oxidation of Rh_2^{4+} to Rh_2^{5+}.[10,25] It is of great interest to determine whether the axial coordination of $^tBuOO^-$ to the diruthenium species plays a key role. These mechanistic issues along with the effects of variation of parameters such as solvent polarity are currently being investigated in our laboratory.

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Supporting Information Available: Detailed syntheses and characterization of $\mathbf{1}\cdot H_2O$ and X-ray crystallographic details (CIF) of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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