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# Ruthenium catalyzed selective oxidation of aryl thiophenes using hydrogen peroxide

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Dedicated to Prof. Bogdan Marciniec on the occasion of his 65th birthday.

**Abstract**

Highly selective catalytic oxidations of (sterically hindered) aryl thiophenes using stoichiometric amounts of hydrogen peroxide (35% in water) and *cis*-Ru(II) bis(substituted phenanthroline) complexes (as low as 0.1%) were carried out in acetonitrile at 75 °C, affording the corresponding sulfones in high yields and selectivities. The products were recovered quantitatively by simple crystallization from the reaction mixture.


*Keywords:* Ruthenium; Oxidation; Thiophenes; Phenanthroline; Homogeneous catalysis

## 1. Introduction

Sulfur-containing diesel oil contaminants are causing increasing concern due to their effects on the atmosphere (acid rains, airborne particulate material) and poisoning of car exhaust catalysts. The US Environmental Protection Agency (EPA), the EU Commission and Japan have launched new regulations to enforce the use of ultra low sulfur diesel fuel, which should not contain sulfur level greater than 15 ppm by year 2006 in the US [1] and 10 ppm in the EU [2] (2009) and Japan (2007). The existing technology towards desulfurised oil is commonly based upon hydrodesulfurisation (HDS), which is achieved in industry by exposing the fuel to a pressure of $H_2$ in the presence of heterogeneous catalysts [3]. Some specific sulfur-containing organic molecules, such as dibenzothiophene (DBT) and derivatives, are however refractory to normal hydrotreating processes, which should be upgraded to work at higher pressures for kinetic and catalyst stability purposes, therefore not being cost-effective.

One of the most promising alternatives to HDS for the removal of benzothiophene (BT) derivatives is considered to be oxidative desulfurisation (ODS), where the sulfur contaminants are converted into the corresponding sulfoxides and sulfones under mild conditions (Scheme 1).

Therefore, the combination of HDS and ODS could be applied to obtain ultra-deeply desulfurised oil in order to match the more and more stringent environmental regulations for automotive diesel. Among the advantages of ODS, are the inverse reactivity of these species to oxidation compared to hydrogenation [4] [4,6-dimethyldibenzothiophene (DMDBT) > 4-methyldibenzothiophene (MDBT) > dibenzothiophene > benzothiophene], the use of cheap and available catalysts and oxidants, the higher selectivity, the easier product separation (precipitation, extraction) and high yields in desulfurised oil [5]. Furthermore, whereas (chiral) sulfoxides find application as pharmaceutical intermediates [6], the selective formation of sulfones usually allows for simple removal by crystallisation due to their strong polarity.

Many approaches to ODS have appeared in the recent literature, focusing on different combinations of catalyst and oxidants. A "synthetic diesel" mixture consisting of significant concentrations of representative sulfur contaminants dissolved in hydrocarbons such as hexadecane is normally used to test the catalytic oxidation protocols. Hydrogen peroxide was found to be the most suitable stoichiometric oxidant, although *t*-BuOOH was also used to oxidise DBT in the presence of Mo catalysts supported on $Al_2O_3$ (16%) [7]. $H_2O_2$ was used

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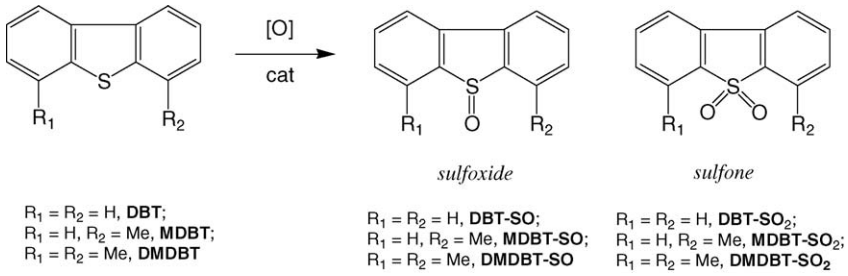



Scheme 1.

together with organic acids to generate peroxoacids [4,8,9], $Na_2WO_4/C_6H_5PO_3H_2/Me(n\text{-octyl})_3NHSO_4$ [10], Mo(VI) and W(VI) catalysts [11], methyltrioxorhenium (MTO) [12,13], polyoxometalates [8], tungstophosphoric acid [14,15], $TiO_2$-supported $V_2O_5$ [16], Pd, $Cr_2O_3$, Mn oxides, $Co–Mo/Al_2O_3$ [17], TS-1, Ti-beta, Ti-HMS [18]. Solid bases such as hydrotalcites and MgLa mixed oxides as catalysts and nitriles or methanol as solvents were also used to oxidise DBT to $DBTSO_2$; the efficiency of the process was hampered by the base-catalyzed $H_2O_2$ unselective decomposition, thus requiring an excess of oxidant [19]. Recently, a high performing (>96% efficiency based on $H_2O_2$), easily recyclable, completely selective protocol for DMDBT oxidation to DMDBT-$SO_2$ using $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst was reported by Li et al. [20] The heteropolyacid catalyst (2.21 μmol) is in this case assembled in emulsion droplets within the diesel phase and can selectively oxidise the sulfur contaminants under mild conditions (30 °C, 20 min for the treatment of 50 mL of real diesel, 0.053 wt% S).

Interestingly, to the best of our knowledge no reports have appeared describing the use of Ru catalysts together with $H_2O_2$. This combination is indeed considered of scarce interest for practical applications, also due to the fact that Ru is known to decompose $H_2O_2$ unselectively, therefore requiring the use of a strong excess of terminal oxidant [21]. Hereby we describe the use of a series of Ru(II) complexes having general formula $[Ru(S)_2(L)_2](PF_6)_2$ [L = 2,9-dimethyl-1,10-phenanthroline (dmp) and S = $H_2O$ (**1**) or S = MeCN (**2**); L = 1,10-phenanthroline-5,6-dione (phedon) and S = $H_2O$ (**3**); L = 2,9-dimethyl-1,10-phenanthroline-5,6-dione ($Me_2$phedon) and S = $H_2O$ (**5**)] as pre-catalysts for the selective oxidation of DMDBT, DBT, BT to the corresponding sulfones in the presence of a *stoichiometric amount* of $H_2O_2$ under mild, neutral conditions (75 °C, 6 h, MeCN) in the absence of PTCs and low catalyst concentrations (down to 0.1%).

## 2. Experimental

All reactions and manipulations were routinely performed under dry nitrogen or argon atmosphere using standard Schlenk techniques. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature on a Bruker ACP 200 (200.13 and 50.32 MHz, respectively). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance ($^1H$) or the deuterated solvent multiplet ($^{13}C$). Gaschromatographic analyses were performed on a Shimadzu GC 14A equipped with a flame ionization detector (FID). Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyzer by the Microanalytical Service of the Department of Chemistry at the University of Florence.

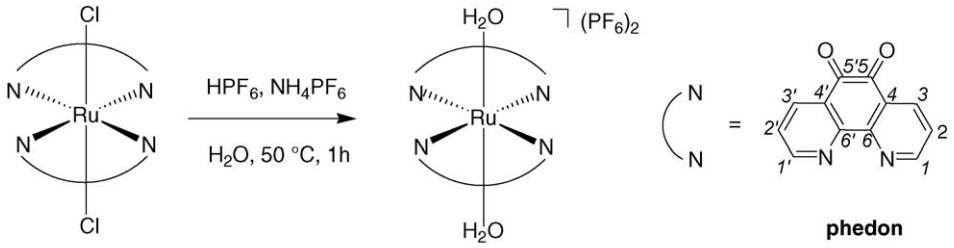
Unless otherwise stated, all solvents were distilled just prior to use from appropriate drying agents. Methanol was distilled from $Mg(OMe)_2$, acetonitrile from $CaH_2$. Deuterated solvents were dried over molecular sieves prior to use. Dibromobenzene was kept over molecular sieves and used as an internal standard for GC purposes. Pure samples to be used as reference for GC measurements were either purchased from Aldrich or synthesized according to the literature [22]. All other chemicals were commercial products and used as received without further purification. Literature methods were employed for the synthesis of 1,10-phenanthroline-5,6-dione (phedon) [23], 2,9-dimethyl-1,10-phenanthroline-5,6-dione ($Me_2$phedon) [24], $[RuCl_2(phedon)_2]\cdot H_2O$ [25], $[RuCl_2(dmp)_2]\cdot H_2O$ [26], $[Ru(H_2O)_2(dmp)_2](PF_6)_2$ [26], and $[Ru(MeCN)_2(dmp)_2](PF_6)_2$ [26]. The complexes were collected as purple solids on a sintered glass-frit and washed before being dried in a stream of nitrogen or under vacuum.

### 2.1. Synthesis of the ruthenium complexes

The new Ru(II) complexes featuring phedon and $Me_2$phedon were synthesized by a modification of the methods reported in the literature for the analogous complexes bearing dmp, phedon or bipyridine [27].

#### 2.1.1. Synthesis of trans-$[Ru(H_2O)_2(phedon)_2](PF_6)_2$ (3)

$[RuCl_2(phedon)_2]\cdot H_2O$ (500 mg; 0.82 mmol) was dissolved in water (50 mL) over a period of 1 h at 50 °C under a $N_2$ atmosphere. 0.5 mL of aqueous 60% $HPF_6$ were added to the stirred solution to dissolve any remaining solid. An excess of solid $NH_4PF_6$ (530 mg; 3.27 mmol) was added, to induce precipitation of the solid product. The mixture was then cooled on an ice bath to complete precipitation of **3**. The solid was collected by filtration and washed with three portions of 0.1 mol/L aqueous 60% $HPF_6$ (2 mL each). The solid was dried in vacuum at 50 °C overnight. Yield: 500 mg, 72%. NMR characterization (numbering for the ligand according to Scheme 2): $^1H$ NMR ($\delta$, $CD_3OD$, 200.13 MHz): 7.90 (dd, 4H, $J_{HH}$ = 4.9 Hz, $J_{HH}$ = 1.8 Hz, H1 and H1′); 8.65 (dd, 4H, $J_{HH}$ = 7.8, 4.9 Hz, H2 and H2′); 9.36 (dd, 4H, $J_{HH}$ = 7.8, 1.8 Hz, H3 and H3′) $^{13}C\{^1H\}$




Scheme 2.

NMR ($\delta$, $CD_3OD$, 50.32 MHz): 126.7 (s, 4C, C2 and C2′); 127.3 (s, 4C, C4 and C4′, nulls in the $^{13}C$ DEPT-135 NMR spectrum); 137.9 (s, 4C, C3 and C3′); 154.3 (s, 4C, C1 and C1′); 165.6 (s, 4C, C6 and C6′); $\delta$ 175.0 (s, 4C, C5 and C5′). Anal. Calcd. for $C_{24}H_{16}F_{12}N_4O_6P_2Ru$: C, 34.02%; H, 1.90%; N, 6.61%. Found: C, 34.55%; H, 2.02%; N, 6.95%.

### 2.1.2. Synthesis of cis-[$RuCl_2(Me_2phedon)_2$]·$H_2O$ (4)

Commercial $RuCl_3{\cdot}3H_2O$ (500 mg; 1.91 mmol), $Me_2$phedon (950 mg; 4.52 mmol) and LiCl (1.2 g; 28.31 mol) were refluxed with magnetic stirring in reagent grade dimethylformamide (5 mL) for 8 h. DMF was then removed in vacuum leaving a deep purple residue, which was dissolved in 50 mL of acetone. The resulting purple solution was then cooled overnight at −16 °C in the freezer giving a dark purple solid, which was separated by filtration and washed with water (5 mL) and diethyl ether (3 × 10 mL). The solid was dried under vacuum. Yield: 835 mg, 65%. NMR characterization (numbering for the ligand according to Scheme 3): $^1H$ NMR ($\delta$, DMSO-$d_6$, 200.13 MHz): 2.82 (s, 6H, $CH_3$); 2.98 (s, 6H, $CH_3$); 8.04 (d, 4H, $J_{HH}$ = 8.6 Hz, H2 and H2′); 8.89 (d, 4H, $J_{HH}$ = 8.6 Hz, H3 and H3′). $^{13}C\{^1H\}$ NMR ($\delta$, DMSO-$d_6$, 50.32 MHz): 26.1 (s, 2C, $CH_3$); 30.2 (s, 2C, $CH_3$); 127.9 (s, 2C, C2 and C2′); 129.2 (s, 2C, C2 and C2′); 131.3 (s, 4C, C4 and C4′, nulls in the $^{13}C$ DEPT-135 NMR spectrum); 138.3 (s, 4C, C3 and C3′), 150.2 (s, 2C, C1 and C1′); 152.7 (s, 2C, C1 and C1′); 167.2 (s, 2C, C6 and C6′); 168.6 (s, 2C, C6 and C6′); 177.3 (s, 4C, C5 and C5′). IR (KBr): $\nu$(Ru–Cl) 520 $cm^{-1}$ (m). Anal. Calcd. for $C_{28}H_{20}Cl_2N_4O_4Ru$: C, 51.86%; H, 3.11%; N, 8.64%. Found: C, 50.65%; H, 3.35%; N, 8.36%.

### 2.1.3. Synthesis of trans-[$Ru(H_2O)_2(Me_2phedon)_2$]($PF_6$)$_2$ (5)

[$RuCl_2(Me_2phedon)_2$]·$H_2O$ (500 mg; 0.75 mmol) was dissolved in water (50 mL) and stirred for 1 h at 50 °C under a $N_2$ atmosphere. The 0.5 mL of aqueous 60% $HPF_6$ were added to the solution to dissolve any remaining solid. An excess of $NH_4PF_6$ (500 mg; 3.07 mmol) was added, to induce precipitation of solid 5. The mixture was then cooled at *ca.* 0 °C with an ice bath to complete precipitation. The solid was collected by filtration, washed with three portions of 0.1 mol/L aqueous $HPF_6$ (2 mL each) and dried in vacuum at 50 °C overnight. Yield: 530 mg, 78%. NMR characterization (numbering for the ligand according to Scheme 4): $^1H$ NMR ($\delta$, $CD_3OD$, 200.13 MHz): 2.95 (s, 6H, $CH_3$); 3.06 (s, 6H, $CH_3$); 8.12 (d, 4H, $J_{HH}$ = 8.3 Hz, H2 and H2′); 8.92 (d, 4H, $J_{HH}$ = 8.3 Hz, H3 and H3′). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_3OD$, 50.32 MHz): 27.3 (s, 2C, $CH_3$); 29.8 (s, 2C, $CH_3$); 128.3 (s, 2C, C2 and C2′); 129.8 (s, 2C, C2 and C2′); 131.6 (s, 4C, C4 and C4′, nulls in the $^{13}C$ DEPT-135 NMR spectrum); 138.1 (s, 4C, C3 and C3′), 152.8 (s, 2C, C1 and C1′); 153.6 (s, 2C, C1 and C1′); 165.3 (s, 2C, C6 and C6′); 167.5 (s, 2C, C6 and C6′); 177.9 (s, 4C, C5 and C5′). Anal. Calcd. for $C_{28}H_{24}F_{12}N_4O_6P_2Ru$: C, 37.22%; H, 2.68%; N, 6.20%. Found: C, 37.25%; H, 2.85%; N, 6.15%.

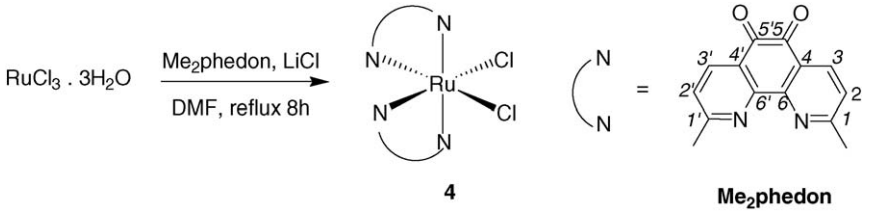
## 2.2. Catalytic oxidation tests

### 2.2.1. Homogeneous tests

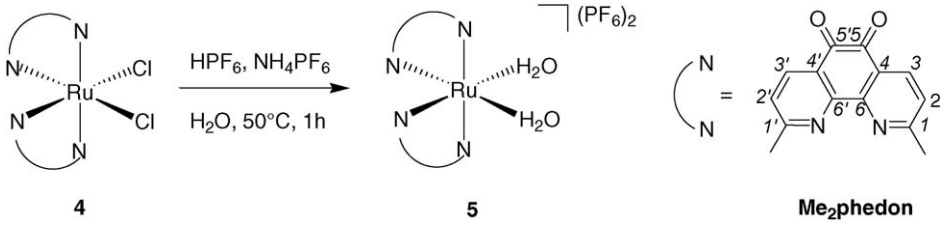
In a typical experiment a solution of the catalyst precursor ($1.2 \times 10^{-2}$ mmol), a 100-fold excess of substrate (1.2 mmol) and dibromobenzene (0.42 mmol) in MeCN (15 mL) was placed under nitrogen into a Schlenk flask closed with a rubber septum. The system was then heated to 75 °C and stirred. Once the temperature stabilized, $H_2O_2$ was syringed into the flask over 3 h, and the reaction mixture was stirred at 75 °C for 3 more hours (6 h total time). Each run was repeated at least twice to ensure reproducibility of the results.

### 2.2.2. Biphasic tests

In a typical experiment, the catalyst precursor ($1.2 \times 10^{-2}$ mmol) was dissolved in water, then the solution was heated up to 75 °C. A solution of dibromobenzene (0.42 mmol) DBT (1.2 mmol) in an organic solvent (nonane, octane or ethyl




Scheme 3.



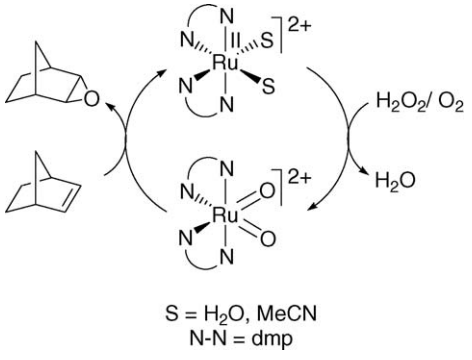

Scheme 4.

acetate) was added into the Schlenk flask containing the aqueous catalyst solution, through a rubber septum, and vigorous stirring immediately began. Once the temperature stabilized, $H_2O_2$ was syringed into the flask over 3 h and the reaction mixture was stirred at 75 °C for 3 more hours (6 h total time). Each run was repeated at least twice to ensure reproducibility of the results.

## 3. Results and discussion

Among the many transition metal catalyzed oxidation protocols able to transfer efficiently oxygen atoms to an organic substrate, ruthenium polypyridyl complexes [28] have shown several adequate characteristics, such as an extensive range of reversible oxidation states (from +2 to +6) and the possibility to form stable oxo complexes such as $[Ru(O)]^{2+}$ and $[Ru(O)_2]^{2+}$ which are known to be good oxygen atom-transfer reagents [29]. In the presence of such precursors, the commonly proposed mechanism involves activation of the Ru(II) precatalyst to either Ru(IV) or Ru(VI) active species via the terminal oxidant, atom transfer of one or two oxygen atoms to the substrate and regeneration of the Ru(II) initial complex to start new turnovers.

Drago and coworkers showed that oxidizing the sterically hindered complex *cis*-$[Ru(dmp)_2(H_2O)_2](PF_6)_2$ (**2**) with $Ce^{4+}$ yielded the putative Ru(VI) complex *cis*-$[Ru(dmp)_2(O)_2](PF_6)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline) which was used as norbornene epoxidation catalyst (Scheme 5) [30]. The catalytic system involves the use of small amounts of $H_2O_2$ (able to generate the Ru(VI) species) and 50 psig $O_2$ in the presence of *cis*-$[Ru(dmp)_2(S)_2](PF_6)_2$ (S = $H_2O$, **1**; MeCN, **2**) at 65–75 °C. Mechanistic details established that *cis*-dioxo stereochemistry is required to obtain an efficient 4-electron transfer catalyst able to exchange both oxygens to the substrate. The use of sterically hindered polypyridyl ligands such as dmp [31] or 6,6′




Scheme 5.

dichloro-2,2′-bipyridine [32] was found to be crucial to inhibit *cis–trans* isomerisation or formation of inactive μ-oxo dinuclear Ru species.

To the best of our knowledge, this kind of catalytic system has never been applied to the selective oxidation of thiophene derivatives to sulfones. Thus, complexes **1** and **2** were synthesized according to the literature to be tested as catalysts for the oxidation of BT, DBT and DMDBT in the presence of $H_2O_2$ as terminal oxidant. Furthermore, novel complexes analogues of **1** and **2** bearing the bifunctional dioxo phenantroline ligands, phedon and $Me_2$phedon (see Section 2), were prepared. The coordination chemistry of phedon [33] and $Me_2$phedon [34] towards Ru and other transition metals has been described, and the electrocatalytic properties and electrochemical behaviour assessed.

The synthesis of $[Ru(H_2O)_2(phedon)_2](PF_6)_2$ (**3**) was carried out starting from the known ruthenium dichloride complex, $[RuCl_2(phedon)_2]\cdot H_2O$ [25]. The NMR characterization is straightforward and clearly confirms the formation of the dicationic species **3**. In the $^1$H NMR spectrum, the three aromatic phedon signals are slightly shifted with respect to the free ligand. The resonance due to the two $H_2O$ ligands, lying in *trans*-axial position, cannot be observed, possibly due to fast and complete deuterium exchange with the NMR solvent $CD_3OD$. The equivalence of the protons might be attributed to the *trans*-diaquo stereochemistry which makes the phedon ligands equivalent, as also confirmed by the $^{13}C\{^1H\}$ spectrum.

For the synthesis of the related Ru(II) complex bearing $Me_2$phedon, it was first necessary to prepare the ruthenium dichloride complex, $[RuCl_2(Me_2phedon)_2]\cdot H_2O$ (**4**) by the plane reaction of $RuCl_3$ with the ligand and a 15-fold excess of LiCl in refluxing DMF. The dichloride does not dissolve in water or methanol, is slightly soluble in acetone, and dissolves in DMF and DMSO.

The $^1$H NMR spectrum in DMSO-$d_6$ shows two aromatic and two aliphatic signals, which in keeping with a *cis*-stereochemistry of the complex (see Scheme 3), suggest a non-equivalent environment for the two $Me_2$phedon ligands. Two singlets at 2.82 and 2.98 ppm are assigned to the methyl substituents of the two phenanthrolines, slightly shifted from the free ligand ($\delta$ 2.87). The doublets at 8.89 and 8.04 ppm correspond to protons H3 and H3′ and H2 and H2′, respectively. The $^{13}C\{^1H\}$ spectrum is in agreement with the assigned structure.

The biscationic species $[Ru(H_2O)_2(Me_2phedon)_2](PF_6)_2$ (**5**) was synthesized following the same procedure used for **3**. Similarly, a brownish-purple solid was isolated after reaction of the dichloride **4** in acidic water ($HPF_6$) and addition of ammonium

Table 1
Catalytic oxidation of DBT using ruthenium-phenanthroline precursors

| Entry | Catalyst Precursor | Catalyst/Substrate | $DBTSO_2$ (%) |
|---|---|---|---|
| 1 | $[Ru(dmp)_2(H_2O)_2]^{2+}$ (**1**) | 1:100 | >99 |
| 2 | $[Ru(dmp)_2(H_2O)_2]^{2+}$ (**1**) | 1:500 | >99 |
| 3 | $[Ru(dmp)_2(H_2O)_2]^{2+}$ (**1**) | 1:1000 | >99 |
| 4 | $[Ru(dmp)_2(MeCN)_2]^{2+}$ (**2**) | 1:100 | 0 |
| 5 | $[Ru(phedon)_2(H_2O)_2]^{2+}$(**3**) | 1:100 | 0 |
| 6 | $[Ru(Me_2phedon)_2(H_2O)_2]^{2+}$ (**5**) | 1:100 | 83 |

Conditions: DBT 1.2 mmol, $N_2$, 75 °C, MeCN (15 mL), 6 h.

hexafluorophosphate to precipitate **5** as $PF_6^-$ salt. At variance with **4**, compound **5** is soluble in water, methanol, acetone and other polar solvents. The $^1H$ and $^{13}C$ NMR spectra indicate that it maintains the geometry of the parent compound **4** with a *cis*-disposition of the two water molecules (see Scheme 4).

### 3.1. Catalytic oxidation tests

The oxidation of dibenzothiophene was chosen as catalyst screening test. The optimized conditions were then established upon evaluation of parameters such as catalyst precursor, presence or absence of an oxygen atmosphere, temperature, and amount of $H_2O_2$ used.

The results of the catalytic tests are summarized in Table 1. Complex **2** does not show any activity for the oxidation of DBT. No colour change of the initially orange solution upon addition of $H_2O_2$ was observed, indicating that **2** likely is not converted into the $Ru(O)_2$ analogue under our conditions. On the other hand, complex **1** does exhibit a colour change to orange, indicative of Ru(VI) species [35], when reacted with $H_2O_2$. The reaction works with a stoichiometric amount of $H_2O_2$ as terminal oxidant under nitrogen. Under an atmospheric pressure of oxygen and substoichiometric quantities of $H_2O_2$, the reaction does not reach complete conversion, meaning that a pressure of $O_2$ may be required for its efficient use as terminal oxidant instead of $H_2O_2$. The optimized conditions for DBT oxidation were found to be substrate/oxidant/catalyst ratios 100/200/1 at 75 °C in MeCN. As expected, complex **3** is not active as oxygen transfer catalyst, confirming that *cis*-dioxo stereochemistry is required; complex **5** is slightly less active than **1**, therefore the latter was chosen for further use being less costly and easier to synthesise from readily available reagents.

As a confirming evidence of the catalytic nature of our results, blank runs (*i.e.* with no catalyst precursor) gave no conversion.

Using a higher substrate:catalyst ratio, namely 500 or 1000, quantitative amounts of $DBTSO_2$ were still produced. The oxidation product precipitates as yellow needle-shaped crystals from the solution upon cooling of the reaction mixture allowing for easy separation and fast recovery of the product.

The oxidation of BT was carried out using the same optimized parameters established for DBT, with complex **1** as catalyst precursor. The selective oxidation of this substrate can in principle be more troublesome, giving the corresponding epoxide (BTE), sulfoxide (BTSO), sulfone ($BTSO_2$), or any of the related mixed compounds (Scheme 6).


Scheme 6.

Under the conditions studied (**1**, $1.2 \times 10^{-2}$ mmol; substrate:catalyst = 100; $H_2O_2$:substrate = 2; 75 °C; MeCN) BT converts quantitatively (>98% yield) into benzothiophene sulfone ($BTSO_2$) with no traces of sulfoxide or epoxide being detected by GC. 4,6-Dimethyl-dibenzothiophene is one of the most refractory compounds towards HDS. In homogeneous reactions, this fact has been attributed to the steric hindrance around the sulfur atom, which is probably blocking the coordination of this one to the metal precursor during the catalytic cycle of HDS. A valid alternative for its removal is indeed ODS, as reported by many authors so far [7–10,16].

The oxidation of DMDBT was carried out using the same optimized parameters already established for DBT with complex **1** as catalyst precursor. Under the studied conditions DMDBT converts quantitatively (>98% yield) to its oxidized derivatives, with both the sulfoxide (8%) and the sulfone (72%) being formed.

The formation of both DMDBT-SO and DMDBT-$SO_2$ is consistent with a mechanism involving at first formation of sulfoxide followed by its oxidation to sulfone, which is at the end of the reaction the most abundant product. In the case of the sterically hindered DMDBT, reaction kinetics allow for the observation of the sulfoxide intermediate. A similar behaviour was already observed by other authors [13].

Some biphasic tests using water as solvent for the catalyst precursor have also been carried out. At temperatures higher than 50 °C, complex **1** is soluble in water. The analogous complexes **3** and **5**, bearing phenanthroline dione ligands, are soluble even at room temperature. The substrates were dissolved in organic solvents such as nonane, octane or ethyl acetate.

Regrettably, no conversion from DBT to $DBTSO_2$ was detected by GC after 6 h of reaction or even longer periods under the optimized conditions described above using complexes **1** and **5** as catalysts. The use of buffered water phase (HOAc/NaOAc 1.0 M, pH 5 and $Na_2CO_3$/$NaHCO_3$ 1.0 M, pH 9.5, 7.5 mL in each case) did not improve the reaction outcome. The reason for this complete lack of catalytic activity could reside in the decreased solubility of the substrate and eventual reaction intermediates (likely the sulfoxides) at higher water contents, hampering correct interphase contact.

## 4. Conclusions

The completely selective oxidation of aryl thiophenes to sulfones was achieved in the presence of Ru(II) precatalysts bearing hindered phenanthrolines, using a stoichiometric amount of $H_2O_2$. Optimized conditions were found to be 1% of catalyst, 75 °C and MeCN as solvent. The catalyst to substrate ratio could be lowered to 0.1% for DBT oxidation without loss of

efficiency in the presence of **1**. The separation of the sulfone from the reaction mixture can be easily achieved by precipitation upon cooling. The use of phenanthroline dione ligands did not improve the catalytic protocol. Further studies are in progress to find the conditions required for the biphasic protocol, such as sonication, mechanical stirring, use of PTCs.

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