EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201301057

Oxo-Rhenium(V) Complexes Containing Heterocyclic Ligands as Catalysts for the Reduction of Sulfoxides

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Keywords: Synthetic methods / Homogeneous catalysis / Reduction / Sulfoxides / Rhenium / Silanes / Boranes

This work reports the catalytic activity of a large variety of oxo-rhenium(V) complexes (1 mol-%) containing the ligands 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta), 2-(2-hydroxyphenyl)benzothiazole (Hhpbt), 2-(2-hydroxyphenyl)benzoxazole (Hhpbo), and 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi) in the deoxygenation of sulfoxides with silanes or boranes as the reducing agents. In general, all of the complexes are excellent catalysts, although the $PhSiH_3$/[$ReOBr_2$(hmpbta)(PPh_3)] and pinacolborane/[$ReOBr_2$(hmpbta)(PPh_3)] systems are the most efficient for the reduction of aromatic and aliphatic sulfoxides and tolerate different functional groups.

Introduction

The reduction (deoxygenation) of sulfoxides to sulfides is a fundamental reaction in both chemistry and biology. This reaction is also frequently employed in natural product and pharmaceutical syntheses that require mild conditions, selectivity, and functional group tolerance. For these reasons, the search for new efficient and chemoselective catalysts for the deoxygenation of sulfoxides is still an important target in organic chemistry.

Among the variety of catalysts used in this reduction,[1] high-valent oxo-molybdenum and oxo-rhenium complexes have attracted considerable interest. These catalytic methods involve the addition of at least one equivalent of a phosphorus compound,[2] silane,[3] borane,[3c,4] hydrogen,[5] or diol[6] as the reducing agent.

In continuation of our studies on the use of high-valent oxo-molybdenum and oxo-rhenium complexes as excellent catalysts for organic reactions,[7] in this work, we explored the catalytic activity of seventeen oxo-rhenium complexes containing different heterocyclic ligands (Figure 1), namely, 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta),[8] 2-(2-hydroxyphenyl)benzothiazole (Hhpbt),[9] 2-(2-hydroxyphenyl)benzoxazole (Hhpbo),[10] and 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi)[11] in the deoxygenation of sulfoxides with silanes and boranes as the reducing agents.

2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta) | 2-(2-hydroxyphenyl)benzothiazole (Hhpbt)

2-(2-hydroxyphenyl)benzoxazole (Hhpbo) | 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi)

Figure 1. Structures of the heterocyclic ligands.

Results and Discussion

To compare the catalytic activity of the seventeen oxo-rhenium complexes of general formula [$ReOX_2$(L)(EPh_3)] (X = Cl, Br; E = P, As) and [ReOBr(hmpbta)$_2$] containing the ligands Hhmpbta, Hhpbt, Hhpbo, and Hhpbi, the reduction of the test substrate 4-methylphenyl sulfoxide was performed with 1 mol-% of these catalysts and $PhSiH_3$ (1.0 mmol) as the reducing agent in tetrahydrofuran (THF) at reflux under air (Table 1). In general, all of the oxo-rhenium complexes tested were highly efficient and afforded excellent yields of the sulfide. Nevertheless, the catalysts containing the ligand Hhmpbta were the most efficient and reduced the sulfoxide in a few minutes (Table 1, Entries 1–4). One exception was the deoxygenation catalyzed by the complex [ReOBr(hmpbta)$_2$], which required more time (6.5 h; Table 1, Entry 5). In contrast, the complexes con-

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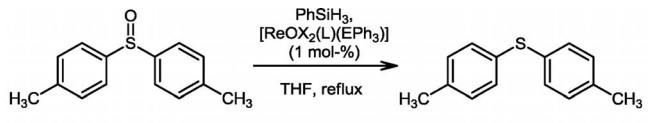
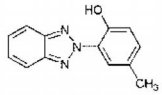
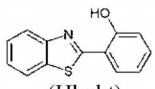
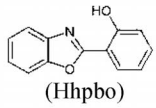
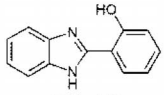
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301057.

taining the ligand Hhpbi were the least effective (Table 1, Entries 14–17). The results also demonstrate that the catalysts with Br ligands (Table 1, Entries 1, 2, 6, 7, 10, 11, and 14) are more reactive then the complexes containing Cl ligands. Finally, no reaction was observed in the absence of catalyst after 24 h (Table 1, Entry 18).

Table 1. Reduction of 4-methylphenyl sulfoxide with $PhSiH_3$ catalyzed by oxo-rhenium complexes.[a]



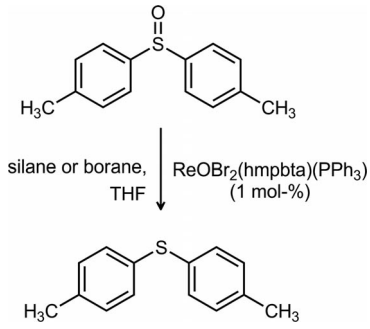
Entry	Catalyst	Ligand	Time	Yield (%)[b]
1	$[ReOBr_2(L)(PPh_3)]$	 (Hhmpbta)	12 min	99
2	$[ReOBr_2(L)(AsPh_3)]$		25 min	99
3	$[ReOCl_2(L)(PPh_3)]$		30 min	98
4	$[ReOCl_2(L)(AsPh_3)]$		33 min	97
5	$[ReOBr(L)_2]$		6 h 30 min	93
6	$[ReOBr_2(L)(AsPh_3)]$	 (Hhpbt)	10 min	90
7	$[ReOBr_2(L)(PPh_3)]$		15 min	96
8	$[ReOCl_2(L)(AsPh_3)]$		50 min	98
9	$[ReOCl_2(L)(PPh_3)]$		2 h	99
10	$[ReOBr_2(L)(PPh_3)]$	 (Hhpbo)	15 min	99
11	$[ReOBr_2(L)(AsPh_3)]$		20 min	99
12	$[ReOCl_2(L)(PPh_3)]$		58 min	96
13	$[ReOCl_2(L)(AsPh_3)]$		2 h 30 min	98
14	$[ReOBr_2(L)(PPh_3)]$	 (Hhpbi)	27 min	98
15	$[ReOCl_2(L)(AsPh_3)]$		4 h	98
16	$[ReOCl_2(L)(PPh_3)]$		24 h	97
17	$[ReOBr_2(L)(AsPh_3)]$		24 h	96
18	without catalyst		24 h	n.r.

[a] The reactions were performed with 1.0 mmol of sulfoxide, 1.0 mmol of $PhSiH_3$, and 1 mol-% of oxo-rhenium complexes. [b] Isolated yields.

The activity of the investigated catalysts is influenced by the electronic properties of both the halide and the chelating ligand. The results revealed that the best electron-donating ability of Br ions has a beneficial influence on the catalytic activity. The lowest catalytic efficiency of the complexes containing the ligand Hhpbi may be correlated with the smallest π-electron-withdrawing power of the imidazole ring. The charge demand of imidazole is one of the smallest among the heteroaromatics and is even smaller than that of the phenyl ring. The higher π-electron-withdrawing power of the triazole, thiazole, and oxazole rings significantly increases the catalytic activity.[12]

The deoxygenation of sulfoxides was explored with different silanes and boranes as reducing agents in the presence of $[ReOBr_2(hmpbta)(PPh_3)]$ (1 mol-%). The silanes studied were phenylsilane, dimethylphenylsilane, triethylsilane, triphenylsilane, and polymethylhydrosiloxane (PMHS). Among these silanes, phenylsilane and PMHS were the most efficient reagents (Table 2, Entries 1, 2, and 4). When the reduction was performed with 1.0 mmol of $PhSiH_3$, the reaction was very fast (12 min), and the prod-

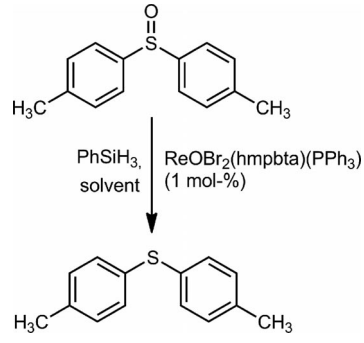
Table 2. Reduction of 4-methylphenyl sulfoxide catalyzed by $[ReOBr_2(hmpbta)(PPh_3)]$ with silanes or boranes as the reducing agent.[a]



Entry	Reducing agent	Reducing agent [mmol]	Temp.	Time	Yield [%][b]
1	$PhSiH_3$	1	reflux	12 min	99
2	$PhSiH_3$	0.3	reflux	40 min	95
3	$PhSiH_3$	1	r. t.	5 h	99
4	PMHS	0.3	reflux	20 min	99
5	$PhMe_2SiH$	1	reflux	24 h	99
6	Et_3SiH	1	reflux	24 h	45
7	Ph_3SiH	1	reflux	24 h	10
8	HBpin	1	reflux	15 min	99
9	HBpin	1	r. t..	24 h	62
10	HBcat	1	reflux	1 h	74
11	–	–	reflux	24 h	5

[a] The reactions were performed with 1.0 mmol of sulfoxide and 1 mol-% of $[ReOBr_2(hmpbta)(PPh_3)]$. [b] Isolated yields.

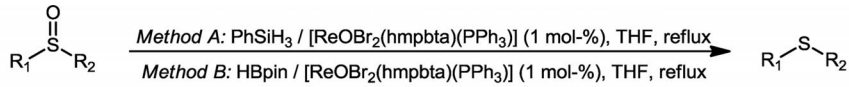
Table 3. Reduction of 4-methylphenyl sulfoxide in different solvents.[a]

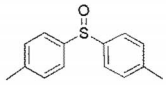
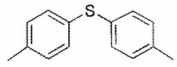
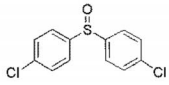
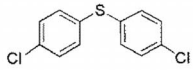
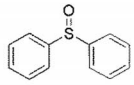
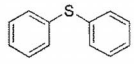
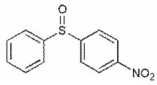
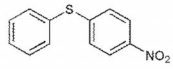
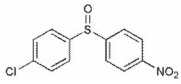
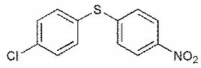
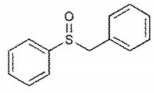
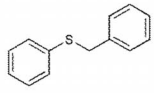
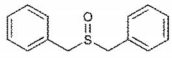
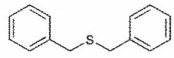
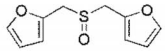
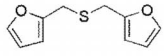
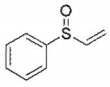
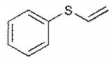
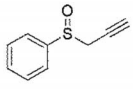
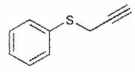
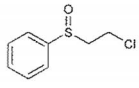
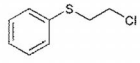
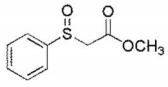
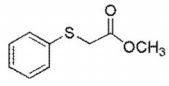
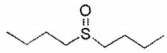
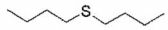


Entry	Solvent	Temp.	Time	Yield [%][b]
1	THF	reflux	12 min	99
2	Toluene	reflux	15 min	96
3	Benzene	reflux	25 min	95
4	$CHCl_3$	reflux	50 min	93
5	CH_2Cl_2	reflux	1 h	97
6	CH_3CN	reflux	24 h	91

[a] The reactions were performed with 1.0 mmol of sulfoxide, 1.0 mmol of $PhSiH_3$, and 1 mol-% of $ReOBr_2(hmpbta)(PPh_3)$. [b] Isolated yields.

Table 4. Reduction of sulfoxides with $PhSiH_3$ or HBpin catalyzed by $ReOBr_2(hmpbta)(PPh_3)$.[a]



Entry	Substrate	Product	Method	Time	Yield (%)[b]	TON/TOF [h^{-1}]
1			A	12 min	99	99/396
2			B	15 min	99	99/396
3			A	25 min	92	92/221
4			B	15 min	97	97/388
5			A	35 min	95	95/163
6			B	20 min	98	98/294
7			A	30 min	93	93/186
8			B	40 min	91	91/136
9			A	25 min	91	91/218
10			B	1 h	98	98/98
11			A	15 min	94	94/376
12			B	30 min	94	94/188
13			A	30 min	95	95/190
14			B	15 min	99	99/396
15			A	30 min	86	86/172
16			B	30 min	77	77/154
17			A	15 min	90	90/360
18			B	15 min	93	93/372
19			A	2 h 30 min	95	95/38
20			B	24 h	89	89/4
21			B	30 min	90[c]	90/180
22			A	1 h 15 min	76	76/61
23			B	30 min	70	70/140
24			A	18 min	80	80/267
25			B	45 min	90	90/120
26			A	30 min	81	81/162
27			B	50 min	70	70/84
28			A	12 min	100[d]	100/500
29			B	18 min	100[d]	100/333
30			A	10 min	100[d]	100/599
31			B	35 min	100[c] [d]	100/172

[a] The reactions were performed with 1.0 mmol of sulfoxide, 1 mol-% of $ReOBr_2(hmpbta)(PPh_3)$, and 1.0 mmol of $PhSiH_3$ or 1.0 mmol of HBpin. [b] Isolated yields. [c] The reaction was performed with 2.0 mmol of HBpin. [d] The conversion was determined by ^1H NMR spectroscopy.

uct was obtained in 99% yield (Table 2, Entry 1). However, when this reduction was performed with only 0.3 mmol of $PhSiH_3$, the reaction required 40 min, and the yield was lower (95%; Table 2, Entry 2). In contrast, at room temperature, the reduction with phenylsilane requires 5 h for completion (Table 2, Entry 3). An excellent yield was also obtained with dimethylphenylsilane, but the deoxygenation required 24 h (Table 2, Entry 5). Moderate-to-low yields of sulfide were isolated when triethylsilane or triphenylsilane was employed (Table 2, Entries 6 and 7).

The deoxygenation of 4-methylphenyl sulfoxide was also studied with the boranes pinacolborane (HBpin) and catecholborane (HBcat; Table 2, Entries 8–10). HBpin (1.0 mmol) was a better reducing agent than HBcat (1.0 mmol) for this reaction at reflux temperature (Table 2, Entries 8 and 10). At room temperature, the reduction with HBpin required more time, and the sulfide was isolated in moderate yield (Table 2, Entry 9). Finally, only 5% yield of sulfide was formed in the absence of reducing agent (Table 2, Entry 11).

The influence of the solvent on the reduction of 4-methylphenyl sulfoxide with phenylsilane catalyzed by 1 mol-% of $ReOBr_2$(hmpbta)(PPh_3) was also studied (Table 3). All of the solvents tested were very efficient for this reduction. Nevertheless, the best solvent was THF, in which the sulfide was obtained in 99% after only 12 min (Table 3, Entry 1). In toluene at reflux temperature, the deoxygenation of the sulfoxide also required 15 min, but the yield of the sulfide was slightly lower (Table 3, Entry 2). Benzene, chloroform, and dichloromethane gave also excellent conversions of sulfide; however, the reactions required more time (Table 3, Entries 3–5). Finally, the reduction in acetonitrile required 24 h (Table 3, Entry 6).

After extensive optimization studies, we explored the reduction of a large variety of sulfoxides with two catalytic systems: $PhSiH_3$/[$ReOBr_2$(hmpbta)(PPh_3)] (1 mol-%) in THF under reflux (Table 4, method A) and HBpin/[$ReOBr_2$(hmpbta)(PPh_3)] (1 mol-%) in THF under reflux (Table 4, method B). Generally, excellent yields of sulfides were obtained with both systems in a few minutes, including sulfides bearing electron-withdrawing or -donating groups. As shown in Table 4, this methodology is equally applicable to diaryl, aryl alkyl, and dialkyl sulfoxides. The high chemoselectivity of this new methodology is shown by the successful reductions of sulfoxides containing several functional groups such as –Cl, $–CO_2R$, $–NO_2$, double or triple bonds, and furfuryl rings with these two catalytic systems.

Comparing these results with our previous work, in which we used the silane/$ReIO_2(PPh_3)_2$ catalytic system for the reduction of sulfoxides,[3a] we conclude that this new method is less efficient. With this system, the reactions require heating at reflux in THF, whereas the reductions with the silane/$ReIO_2(PPh_3)_2$ system can be performed at room temperature. However, this new silane/[$ReOBr_2$(hmpbta)(PPh_3)] catalytic system is more efficient than the silane/MoO_2Cl_2 (5 mol-%) method, which requires a higher amount of oxo-molybdenum complex, reflux temperature, longer reaction times, and inert atmosphere.[3b]

In comparison with other methodologies reported in the literature for the reduction of sulfoxides with silanes as reductants, we conclude that the silane/[$ReOBr_2$(hmpbta)(PPh_3)] (1 mol-%) system is more efficient than the $PhSiH_3$/$Zn(OTf)_2$ (5 mol-%)[3d] and $PhSiH_3$/[$Mo_2(OR)_6$] (1 mol-%) systems[3e] and requires shorter reaction times and/or less catalyst. This new silane/[$ReOBr_2$(hmpbta)(PPh_3)] system also has better turnover numbers (TONs) and turnover frequencies (TOFs) than the methodologies reported in the literature.[3]

On the basis of DFT calculations preformed for our previous work,[4c] we proposed a similar mechanism for the reduction of sulfoxides catalyzed by [$ReOBr_2$(hmpbta)(PPh_3)] (Figure 2), which should start with the coordination of a molecule of sulfoxide to the metal center by substitution of triphenylphosphine to form [$ReOBr_2$(hmpbta)(R_2SO)] (**2**). In the next step, the reducing agent (silane or borane) reacts with this species to give a hydride complex **3**, as a result of the addition of the Si–H or B–H bond to the oxo-rhenium bond. Then, the reduction of the sulfoxide should occur with liberation of the sulfide and a molecule of HOR (R = Bpin or $SiPhH_2$) to give $ReOBr_2$(hmpbta) **5**. Finally, a new molecule of sulfoxide coordinates to the metal center to regenerate the oxo-rhenium complex **2**.

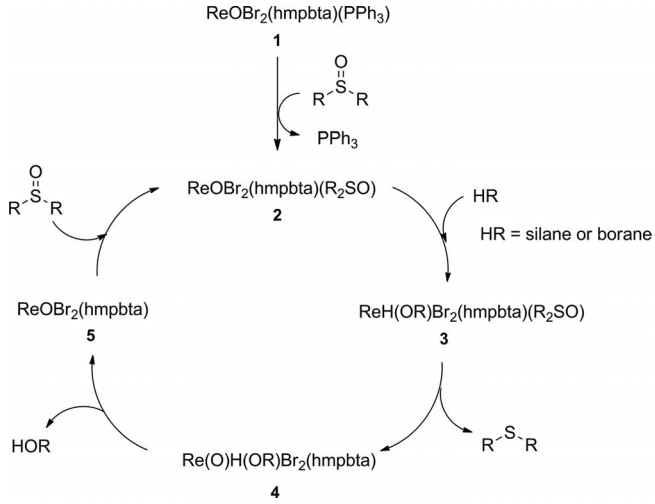


Figure 2. Proposed mechanism for the reduction of sulfoxides catalyzed by [$ReOBr_2$(hmpbta)(PPh_3)] with silanes or boranes as the reducing agent.

Conclusions

We have demonstrated that oxo-rhenium complexes containing the ligands Hhmpbta, Hhpbt, Hhpbo, and Hhpbi are highly efficient catalysts for the deoxygenation of 4-methylphenyl sulfoxide with $PhSiH_3$ as the reducing agent. We have also developed a simple and very efficient method for the reduction of a large variety of sulfoxides with excellent yields and high chemoselectivity with the $PhSiH_3$/[$ReOBr_2$(hmpbta)(PPh_3)] and HBpin/[$ReOBr_2$(hmpbta)(PPh_3)] catalytic systems. These two methodologies have other remarkable advantages such as low catalyst loading

(1 mol-%), fast reaction times, clean reactions, and catalyst stability towards air and moisture, which allows the reactions to be performed under air.

We believe that these new methods can be useful alternatives to the other methods described in the literature and can also bring great benefits to both academia and industry for the production of fine chemicals such as bioactive and pharmaceutical compounds.

Further studies to explore the catalytic activity of other oxo-rhenium complexes as well to extend this methodology to the deoxygenation of other substrates are now under investigation in our group.

Experimental Section

General Procedure for the Reduction of Sulfoxides with $PhSiH_3$ or HBpin Catalyzed by [$ReOBr_2$(hmpbta)(PPh_3)]: To a solution of catalyst (1 mol-%) and sulfoxide (1.0 mmol) in THF (3 mL) was added $PhSiH_3$ (1.0 mmol) or HBpin (1.0 mmol). The reaction mixture was stirred at reflux temperature under air, and the progress of the reaction was monitored by TLC or ^1H NMR spectroscopy. Upon completion, the reaction mixture was evaporated and purified by silica gel column chromatography with *n*-hexane to afford the sulfides.

Supporting Information (see footnote on the first page of this article): Characterization data and ^1H and $^{13}C\{^1H\}$ NMR spectra for all products.

Acknowledgments

This research was supported by Fundação do Ministério de Ciência e Tecnologia (FCT) through project PTDC/QUI-QUI/110080/2009. S. C. A. S. (SFRH/BD/63471/2009) and J. R. B. (SFRH/BD/90659/2012) thank FCT for grants. M. W. thanks the Polish National Science Centre for a grant (UMO-2011/03/N/ST5/04522). The authors thank the project PEst-OE/QUI/UI0100/2013 and the Portuguese NMR Network (IST-UTL Center) for providing access to the NMR facilities.

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Received: July 16, 2013
Published Online: January 17, 2014

