Tetrahedron Letters 56 (2015) 414–418

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Reduction of aldehydes catalyzed by oxo-rhenium(V) complexes containing heterocyclic ligands

Joana R. Bernando [a], Pedro R. Florindo [a], Mariusz Wolff [b], Barbara Machura [b], Ana C. Fernandes [a,*]

[a] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[b] *Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland*

ARTICLE INFO

Article history:
Received 1 September 2014
Revised 20 November 2014
Accepted 26 November 2014
Available online 3 December 2014

Keywords:
Oxo-rhenium complexes
Reduction
Aldehydes
Silanes

ABSTRACT

This work describes the catalytic activity of several oxo-rhenium complexes containing the heterocyclic ligands 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta), 2-(2-hydroxyphenyl)benzothiazole (Hhpbt), 2-(2-hydroxyphenyl)benzoxazole (Hhpbo), 2-(2-hydroxyphenyl)-1*H*-benzimidazole (Hhpbi), isoquinoline-1-carboxylic acid (iqcH), and 4-methoxy-2-quinolinecarboxylic acid (mqcH) in the reduction of 4-nitrobenzaldehyde using phenylsilane as reducing agent. In general, all of the catalysts tested gave good to excellent yields of the 4-nitrobenzyl alcohol. Although, the best result was obtained with the catalytic system $PhSiH_3/[ReOBr_2(hmpbta)(PPh_3)]$ (5 mol %). This system was also applied to the reduction of a large variety of aldehydes, producing the corresponding primary alcohols in good to excellent yields and good chemoselectivity.

The selective reduction of carbonyl groups is an important transformation in chemistry and represents a challenge in both chemical and pharmaceutical industries. In particular, benzylic alcohols occupy an important position in organic synthesis as target molecules of biological interest and synthetic intermediates. For these reasons, the development of new methodologies for the chemoselective reduction of carbonyl groups remains a challenge in organic synthesis.

In 2003 Toste and co-workers have demonstrated that the high valent oxo-rhenium complex $ReIO_2(PPh_3)_2$ was an excellent catalyst for the hydrosilylation of aldehydes and ketones to the corresponding silyl ethers using silanes as reducing agents.[1] Since then, several studies were reported in the literature for the hydrosilylation and for the reduction of the carbonyl group to the corresponding alcohols catalyzed by several oxo-rhenium and oxo-molybdenum complexes.[2–9]

In our previous works, we have demonstrated that several oxo-rhenium complexes containing the heterocyclic ligands Hhmpbta, Hhpbt, Hhpbo, and Hhpbi were excellent catalysts for the direct reductive amination of aldehydes, producing secondary and tertiary amines in good to excellent yields[10] and also for the deoxygenation of a large variety of sulfoxides using silanes and boranes as reducing agents.[11]

In continuation of our studies on the use of oxo-molybdenum and oxo-rhenium complexes as excellent catalysts for organic reductions,[12] in this work we explore the catalytic activity of several oxo-rhenium complexes with general formula $[ReOX_2(L)(PPh_3)](X = Cl, Br)$, containing different heterocyclic ligands (Fig. 1), namely, 2-(2-hydroxy-5-methylphenyl)benzotriazole (Hhmpbta),[13] 2-(2-hydroxyphenyl)benzothiazole (Hhpbt),[14] 2-(2-hydroxyphenyl)benzoxazole (Hhpbo),[15] and 2-(2-hy-droxyphenyl)-1*H*-benzimidazole (Hhpbi),[16] isoquinoline-1-carboxylic acid (iqcH),[17] and 4-methoxy-2-quinolinecarboxylic acid (mqcH)[17] in the reduction of carbonyl compounds using silanes as reducing agents.

To compare the catalytic activity of these oxo-rhenium complexes, the reduction of the test substrate 4-nitrobenzaldehyde was performed with $PhSiH_3$ (2 mmol) in reflux of THF under air atmosphere, followed by deprotection of the resulting silyl ether with TBAF, affording the 4-nitrobenzyl alcohol (Table 1). In general, all of the oxo-rhenium complexes tested were efficient and produced good to excellent yields of 4-nitrobenzyl alcohol. Nevertheless, the catalysts containing the ligand Hhmpbta were the most efficient (Table 1, entries 1 and 5).

The best result was obtained with the catalyst $[ReOBr_2(hmpbta)(PPh_3)]$ (5 mol %), affording the 4-nitrobenzyl alcohol after 13 min in 93% yield at reflux of THF (Table 1, entry 1). Similar reduction performed at room temperature produced the alcohol in 78% yield after 24 h (Table 1, entry 2). Using only 3 mol % or 2 mol % of this oxo-rhenium complex, the 4-nitrobenzyl alcohol was obtained in 78% and 76% yields, respectively (Table 1, entries 3- and 4). The reduction carried out in the presence of $[ReOCl_2(hmpbta)(PPh_3)]$ (5 mol %) also gave the alcohol in excellent yields (91%) after 1 h

---

[*] Corresponding author. Tel.: +351 218419264; fax: +351 218464455.
E-mail address: anacristinafernandes@tecnico.ulisboa.pt (A.C. Fernandes).

http://dx.doi.org/10.1016/j.tetlet.2014.11.119
0040-4039/© 2014 Elsevier Ltd. All rights reserved.

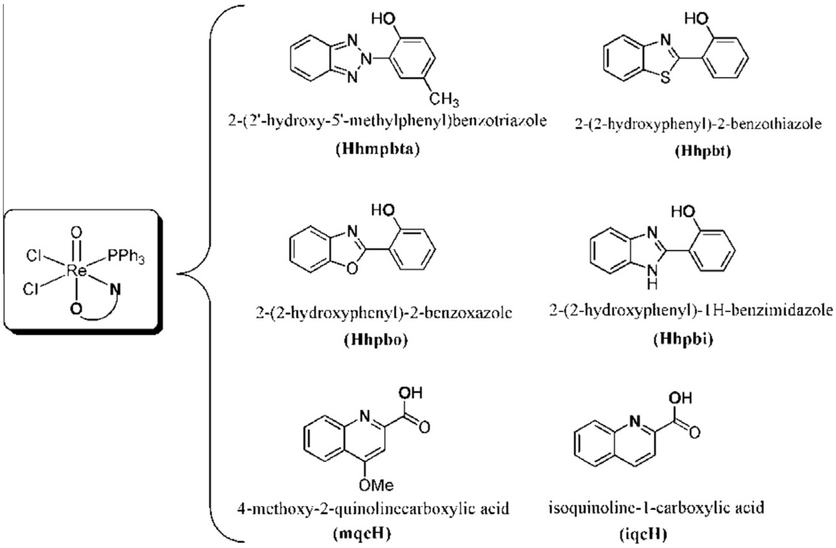
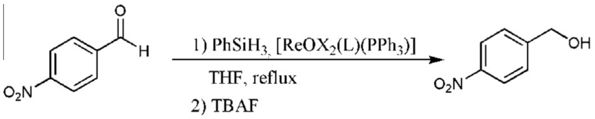
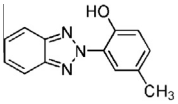
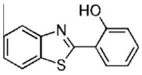
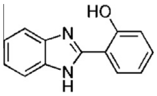
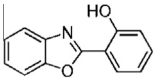
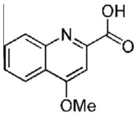
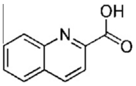


Figure 1. Structures of oxo-rhenium complexes and ligands O–N.

Table 1

Reduction of 4-nitrobenzaldehyde with PhSiH$_3$ catalyzed by oxo-rhenium complexes with the general formula [ReOX$_2$(L)(PPh$_3$)](X = Cl, Br)[a]



Entry	Catalyst	Ligand		Temp (°C)	Time	Yield (%)[b]
1	[ReOBr$_2$(L)(PPh$_3$)]	 **Hhmpbta**	5	Reflux	13 min	93
2	[ReOBr$_2$(L)(PPh$_3$)]		5	rt	24 h	78
3	[ReOBr$_2$(L)(PPh$_3$)]		3	Reflux	20 min	78
4	[ReOBr$_2$(L)(PPh$_3$)]		2	Reflux	30 min	76
5	[ReOCl$_2$(L)(PPh$_3$)]		5	Reflux	1 h	91
6	[ReOBr$_2$(L)(PPh$_3$)]	 **Hhpbt**	5	Reflux	2 h	79
7	[ReOCl$_2$(L)(PPh$_3$)]		5	Reflux	1 h	84
8	[ReOCl$_2$(L)(PPh$_3$)]	 **Hhpbi**	5	Reflux	2 h 30 min	81
9	[ReOBr$_2$(L)(PPh$_3$)]	 **Hhpbo**	5	Reflux	30 min	80
10	[ReOCl$_2$(L)(PPh$_3$)]	 **mqcH**	5	Reflux	1 h 20 min	79
11	[ReOCl$_2$(L)(PPh$_3$)]	 **iqcH**	5	Reflux	1 h 15 min	77
12	Without catalyst	—	—	Reflux	24 h	No reaction

[a] The reactions were carried out with 1.0 mmol of aldehyde, 2.0 mmol of PhSiH$_3$, and 1.0 mmol of TBAF.

[b] Isolated yields.

(Table 1, entry 5). Finally, no reaction was observed in the absence of catalyst after 24 h (Table 1, entry 12).

The reduction of 4-nitrobenzaldehyde was investigated with different silanes as reducing agents catalyzed by [ReOBr$_2$(hmpbta)(PPh$_3$)] (5 mol %). The best result was obtained with 2 mmol of PhSiH$_3$ at reflux temperature of THF, affording the 4-nitrobenzyl alcohol in 93% yield after 13 min (Table 2, entry 1). Similar reaction performed at room temperature produced the alcohol in 78% yield