

Oxidation of Alcohols Catalyzed by Ruthenium (III) Complex Synthesized from Schiff Bases

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Oxidation of alcohols to aldehydes and ketones is a classical reaction in organic chemistry and an important methodology in organic synthesis. The conservative approach involve the use of metallic super oxidants,¹ extremely toxic and not selective reagents such as CrO₃, PCC, KMnO₄, or even the mild and sophisticated Dess-Martin or Swern reaction, but all these methodologies are stoichiometric. There are also several catalytic oxidative processes and ruthenium is the most useful catalyst.² The main goal of this work was the synthesis of ruthenium complexes from Schiff bases and analogues to evaluation of their catalytic activities for the oxidation of alcohols to aldehydes and ketones. The complexes **1** to **6** were prepared using the corresponding nitrogenated ligands and ruthenium (III) chloride, in yields between 42% and 65%, Figure 1. The ruthenium compounds **1** to **6** were applied as catalysts in the oxidation of alcohols, following methodology adapted from Chatterjee *et al.*,³ employing *tert*-butylhydroperoxide (TBHP) as co-oxidant, a phase transfer catalyst (PTC) and 1 mol% of the metallic complexes. On

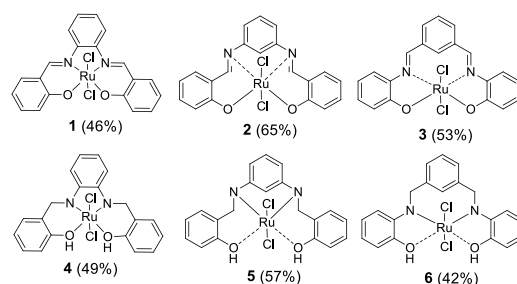
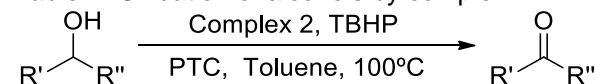


Figure 1. Ruthenium (III) complexes from Schiff bases and analogues.

these conditions all the synthesized complexes showed catalytic activity for the oxidation of benzylic alcohol, used as substrate model. Using the complex **2** the parameters such as solvent, temperature, and reaction time were optimized and a set of alcohols was carefully selected and submitted for oxidation. On table 1 are shown the results using complex **2**, but all the six ruthenium complexes were evaluated and their kinetics monitored and compared by GC-MS.

Table 1. Oxidation of alcohols by complex 2



Oxidation Product	Time (min)	Yield (%)
3-nitrobenzaldehyde	10	100
4-nitrobenzaldehyde	10	100
3-anisaldehyde	30	84
4-anisaldehyde	30	71
4-fluorbenzaldehyde	30	86
4-bromobenzaldehyde	30	84
1-naphthaldehyde	30	94
2-naphthaldehyde	30	91
Furfuraldehyde	30	79
2-nitrofurfuraldehyde	30	93
Cyclohexanemethanaldehyde	30	8
Hexanal	60	5
Acetophenone	40	42
4-methoxyacetophenone	40	25
Cyclohexanone	40	20

¹ TOJO, G., FERNÁNDEZ, M. I. **Oxidation of alcohols to aldehydes and ketones: a guide to current common practice.** Springer Science & Business Media, 2006.

² MURAHASHI, S. **Ruthenium in organic synthesis.** John Wiley & Sons, 2006.

³ CHATTERJEE, D., MITRA, A. *Journal of Coordination Chemistry*, 57, 175-182, 2004.

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