

Chiral Mo and W Complexes bearing Oxazoline-Cyclopentadienyl Ligands

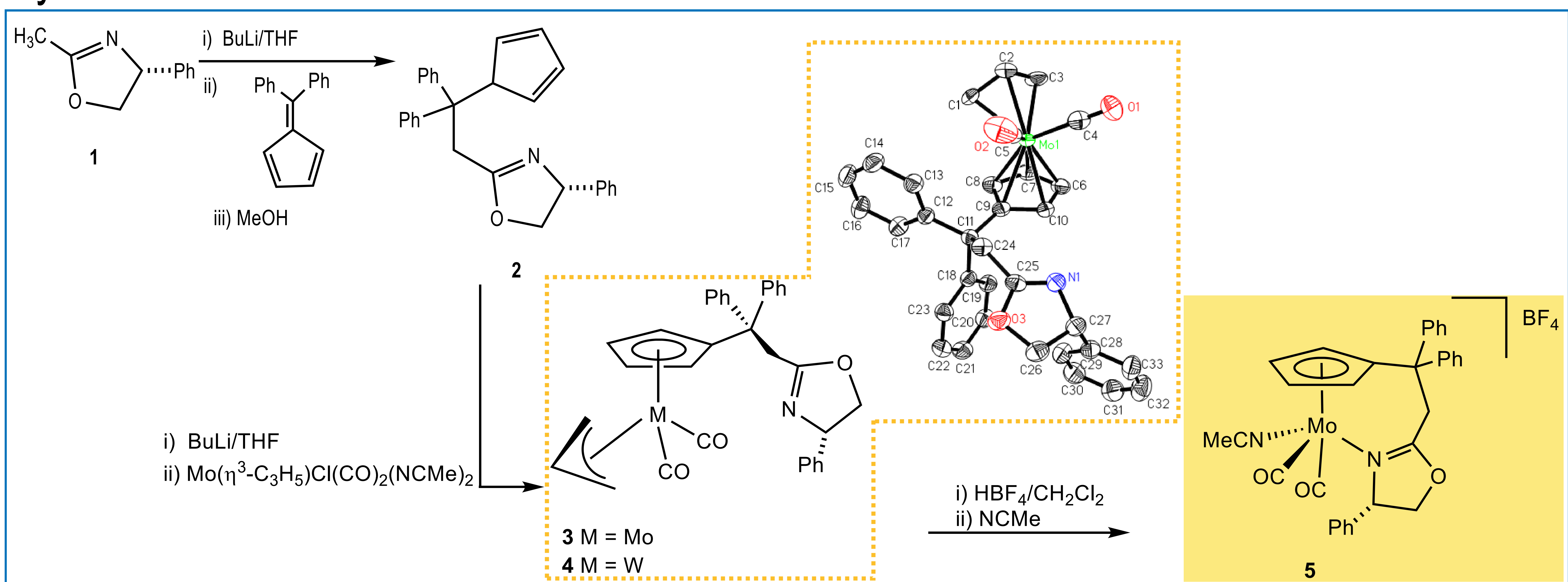
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Introduction

CpMO₂R and CpM(CO)₃R are excellent catalysts for the epoxidation of olefins with TBHP¹ and sulfoxidation with TBHP or H₂O₂.² We became interested in developing chiral Cp-based catalysts for use in the asymmetric version of these reactions and recently prepared *ansa*-(Cp-NHC)Mo(CO)₂I derivatives (NHC=N-heterocyclic carbene).³ Here we report the synthesis of a new bidentate cyclopentadienyl-oxazoline ligand (Cp^{ox}) and its coordination to Mo and W, to afford chiral complexes that have been applied as catalysts in the olefin epoxidation and carbonyl group hydrosilylation.

Synthesis



Catalysis

Table 1. Olefin epoxidation by 3 - 5 and TBHP^a or H₂O₂^b

Cat.	Olefin	Oxidant	t	Yield (%) ^c
3	<i>cis</i> -Cyclooctene	TBHP	45 min	96
3	(<i>R</i>)-Limonene	TBHP	1 h	100 (50/50)
3	<i>trans</i> -β-Methylstyrene	TBHP	16 h	58 (ee ≤ 5%)
4	<i>cis</i> -Cyclooctene	H ₂ O ₂	2 h	88
5	<i>cis</i> -Cyclooctene	TBHP	30 min	98
5	<i>cis</i> -Cyclooctene	H ₂ O ₂	11 h	92
5	(<i>R</i>)-Limonene	TBHP	1 h	100 (60/40)

^acat:subst:oxidant 1:100:200, in CHCl₃, at 55 °C; ^bin NCMe, at 70°C; ^cby GC; in parentheses, trans/cis ratio.

Table 2. Hydrosilylation of carbonyl catalyzed by 5^a

Substrate	t (h)	Yield (%) ^b
	3	≥99
	2	≥99
	7	≥99
	24	0

^acat:subst:silane 1:100:120, in NCMe, at 80 °C; ^bby ¹H NMR

Conclusions

The bidentate cyclopentadienyl-oxazoline complex [Cp^{ox}Mo(CO)₂(NCMe)]BF₄ (**5**) is an efficient catalyst in olefin epoxidation, with TBHP and H₂O₂. The intramolecular coordination of the oxazoline moiety was expected to create asymmetric induction, but negligible e.e. is observed (probably due to ligand decoordination). This is one of the first reports of catalytic activity of cyclopentadienyl Mo(VI) oxo (or carbonyl) complexes using H₂O₂. **5** is also highly active in the hydrosilylation of aldehydes. No reaction was observed using ketones (and consequently, we could not examine the capability of the catalyst in asymmetric induction).

References

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Acknowledgments

We acknowledge financial support from FCT, POCI 2010, and FEDER through project PTDC/QUI-QUI/098682/2008, REDE/1517/RMN/2005 and REDE71504/REM/2005. CG thanks EST-IPS for a short duration grant. PR and JB thank FCT for grants.