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A novel catalyst for alkene epoxidation: a polymer-supported $Co^{II}LCl_2$ {L = 2-(alkylthio)-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4*H*-imidazole-4-one} complex

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Abstract—A polymer-supported complex based on 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin has been synthesized and employed as a catalyst for the epoxidation of alkenes using iodosylbenzene and hydrogen peroxide as oxidants.

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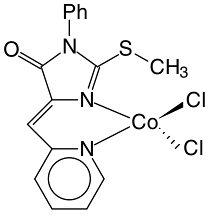
Epoxidation reactions are important transformations of olefins, because epoxides are versatile electrophilic intermediates in organic synthesis.[1] In the ongoing pursuit to develop environmentally benign synthetic methodologies there is currently great interest in new and more efficient catalytic versions of these oxidations.[2] The use of transition metal complexes as the epoxidation catalysts is of particular interest, due to their ability to activate oxidants such as molecular oxygen, iodosylarenes and H_2O_2.[1] Compared to catalytic methods that require oxidants like NaOCl and ammonium periodate, the use of H_2O_2 offers the advantages, that it is cheap, environmentally friendly, and that it is a readily available and abundant reagent. Since water is the only expected by-product, synthetic applications of this reagent are undoubtedly appealing provided efficient catalysis can be accomplished.[2,3] Also such catalytic systems allow epoxidations to be carried out under mild conditions and exhibit high degrees of selectivity.[4]

In the present work, we synthesized a novel Co(II)-complex capable of catalysing epoxidation of alkenes under homogeneous (in solution) and heterogeneous conditions.

The application of polymer-supported catalysis in organic transformations has received considerable attention in recent years. Immobilization of homogeneous catalysts on polymeric supports offers the practical benefits of heterogeneous catalysis whilst retaining the advantages of homogeneous catalytic reactions. Some of the attractive features of polymer-supported catalysis are easy separation of the catalyst from reagents and reaction products, simplification of the methods of recycling the catalysts, the non-volatility and non-toxic characteristics imparted to metal complexes while anchored to high molecular weight polymer backbones, and minimization of catalyst deactivation pathways by site isolation.[5]

Earlier, we have reported that the reaction of 2-(methylthio)-3-phenyl-5-(pyridine-2-ylmethylene)-3,5-dihydro-4*H*-imidazole-4-one with $CoCl_2 \cdot 6H_2O$ in CH_2Cl_2–MeCN solution resulted in the formation of the complex $CoLCl_2 \cdot 0.5MeCN$ (**1**).[6]



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Keywords: Catalysis; Epoxides; Alkenes; Cobalt(II); 2-(Alkylthio)-3,5-dihydro-4*H*-imidazole-4-one complexes; Polymer-supported complexes.

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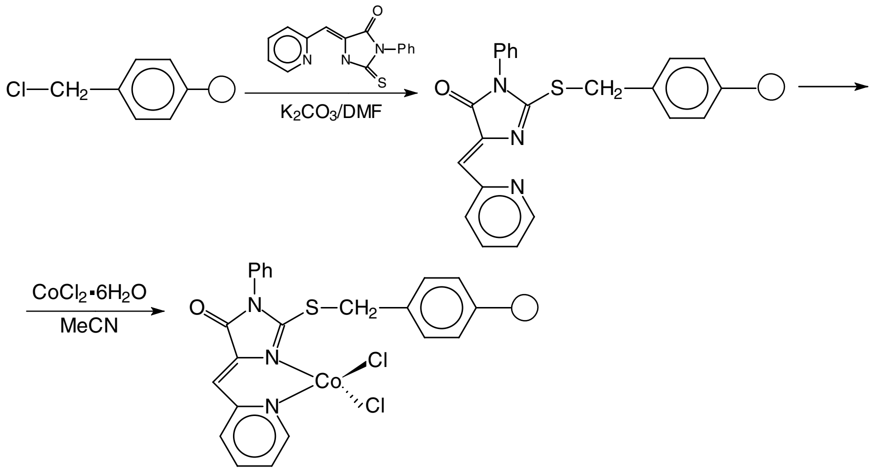
Cobalt(II) complexes are useful catalysts for alkene epoxidation as cobalt(II) appears to be the oxygen transmitting agent. For instance, the β-diketonate complex, $Co^{II}(acac)_2$,[7] cobalt phthalocyanines[8] and others on polyaniline-support have been prepared and used for the aerobic epoxidation of alkenes.

In this study, we investigated the attachment of metal complex **1** to a polymer support as shown in Scheme 1.

The reaction conditions are given below.[9] The structure of the polymer-supported complex **2** was determined by IR spectroscopy.



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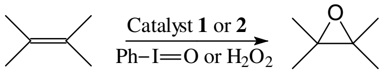
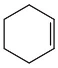
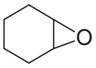
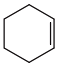
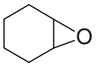
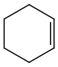
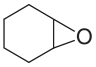
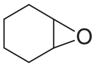
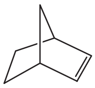
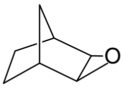
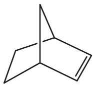
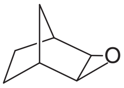
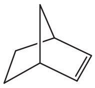
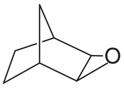
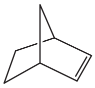
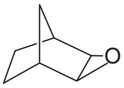
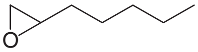
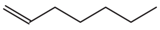
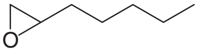
Scheme 1.

Table 1. Epoxidation of olefins with iodosylbenzene and hydrogen peroxide in the presence of catalysts **1** or **2**[a]



Entry	Alkene	Oxidant	Catalyst	Product	Yield (%)
1		Ph–I=O	**1**		40
2		Ph–I=O	**2**		70
3		H_2O_2	**1**		44
4		H_2O_2	**2**		73
5		Ph–I=O	**1**		38
6		Ph–I=O	**2**		71
7		H_2O_2	**1**		74
8		H_2O_2	**2**		65
9		H_2O_2	**1**		10
10		H_2O_2	**2**		85

[a] See Ref. 10 for typical reaction conditions.

The catalytic activity of complexes **1** and **2** in the epoxidation of alkenes was investigated. The reactions were conducted using iodosylbenzene and hydrogen peroxide as sources of oxygen (Table 1).

It should be emphasized that when using norbornene as the substrate, formation of only the *exo*-isomer was observed according to the ^{1}H NMR spectroscopy.

To summarize, the polymer-supported cobalt(II) complex **2** generated from 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin in two steps has been utilized for the epoxidation of alkenes with moderate yields. The catalytic activity of the cobalt(II) complex **1** and the polymeric cobalt(II) complex **2** has been investigated and it was shown that the polymeric analogue exhibits greater efficiency, especially when using H_2O_2 as the oxidant.

Currently, we are investigating the possibility of stereoselective alkene epoxidation using analogous Co(II) complexes with chiral ligands.

References and notes

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9. Typical reaction procedure: The functionalized polystyrene resin (0.5 mmol) was added to a solution of the potassium salt of 3-phenyl-5-(2-pyridylmethylidene)-2-thiohydantoin (0.5 mmol) in DMF. The modified polystyrene resin obtained (0.15 mmol) was added to a solution of $CoCl_2{\cdot}6H_2O$ in MeCN. In both cases, the reaction mixture was stirred at room temperature for 4–5 h. The precipitates obtained were filtered and washed with diethyl ether and dried in air.
10. Typical reaction procedure: (a) To a solution of the alkene (1 equiv) and Ph–I=O (0.2 equiv) in MeCN the catalyst **1** or **2** (0.02 equiv) was added. The reaction mixture was stirred at room temperature for 4 h. The catalyst was separated from the reaction mixture by flash chromatography or filtering when using complexes **1** and **2**, respectively. (b) To a solution of the alkene (1 equiv) and H_2O_2 (1 equiv) in MeCN the catalyst **1** or **2** (0.1 or 0.03 equiv, respectively) was added. The procedure outlined above was then followed.