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Polypyrazolylborate copper(I) complexes as catalysts of the homogeneous and heterogeneous styrene epoxidation reaction

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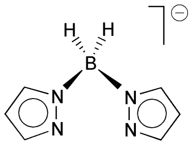
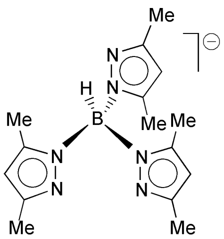
The complexes BpCu (1) and Tp*Cu (2) catalyse the transformation of styrene into styrene oxide using Oxone as the oxidising agent; the use of silica gel-supported 1 or 2 as heterogeneous catalysts affords similar results, using water as the sole solvent.

Copper complexes have been extensively used as catalysts in metal-induced carbene transfer reactions to olefins to give cyclopropanes.[1] Their use in olefin aziridination reactions has also been frequently reported in the last decade.[1] By contrast, very few chemical systems based on this element are known to promote the oxidation of an olefin into the corresponding epoxide:[2–7] most of them have been developed with cyclic or strained olefins (thus avoiding undesired, side-reactions), and their catalytic capabilities are not as yet comparable to those of well-known catalysts based on manganese–salen or iron–porphyrin complexes.[8] For example, Cu(II) salicylaldehyde derivatives have been reported in the epoxidation of alkenes with molecular oxygen and 2-methylpropanal, the yields being found in the 22–40% range.[3] Murahashi and co-workers have reported the use of copper salts for a similar transformation, but in this case the yields were considerably higher (80–90%).[5] Cu(TPP) and Cu(cyclam)$^{2+}$ have also been used[2] in the epoxidation of cyclohexene with oxygen and aldehydes, with low to moderate yield, although the participation of metal-oxo intermediates in the epoxide formation pathway could not be established. In the last few years, we have focused our attention on the use of polypyrazolylborate[9] copper(I) complexes as catalysts for olefin cyclopropanation and aziridination reactions under homogeneous conditions,[10,11] and we have also developed their immobilization by supporting the catalyst precursors on silica gel, thus achieving the heterogenisation of the homogeneous system.[12] We have now studied the use of the complexes BpCu (**1**) and Tp*Cu (**2**) (Bp = dihydridobispyrazolylborate; Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) as the catalyst precursors in the epoxidation reaction under both homogeneous and heterogeneous conditions, and we have discovered that these Cu(I) complexes also display catalytic activity towards this transformation. Complex **1** was reported by Bruce as a 14-electron compound.[13] Although its solid state structure is unknown, molecular weight studies revealed the existence of discrete BpCu units in solution. Complex **2** was reported by Ibers and co-workers:[14] its solid state structure was determined by X-ray as a dimeric compound [Tp*Cu]$_2$, but in solution the mononuclear species Tp*Cu prevailed. Thus, both complexes **1** and **2** seem to display monomeric structures when dissolved.

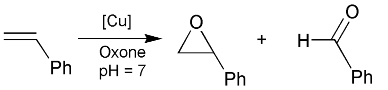


$H_2B(pz)_2$, Bp



HB(pz*)$_3$, Tp*

The addition of an aqueous solution of potassium peroxymonosulfate (Oxone = $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) neutralised with $NaHCO_3$, to an acetonitrile solution containing the styrene and the catalyst precursors BpCu or Tp*Cu led to the conversion of the olefin into a mixture of mainly styrene oxide and benzaldehyde (eqn. 1, Table 1)†. The overall yield, based on oxidant, was nearly 70% for BpCu and 60% for Tp*Cu, of which at least 85–90% corresponded to styrene oxide (60 and 50% respectively, based on oxidant). Other minor products, including benzoic acid, accounted for *ca*. 5%. These conversion rates are clearly an improvement over most of those obtained with the copper-based epoxidation systems known to date.[2–5] In addition, no phase-transfer catalyst has been added to the biphasic reaction mixture, unlike the common procedure employed in related systems.[15]



(1)

The formation of benzaldehyde in metal-induced olefin oxidation was reported by Groves *et al*.[16] with an iron–porphyrin complex as catalyst. However, it is worth mentioning that control experiments have also shown the formation of benzaldehyde when reacting styrene oxide and Oxone in the absence of the copper complexes, as well as the oxidation of benzaldehyde to benzoic acid under the same conditions. This is in agreement with recent results from Corma and co-workers with Ti-zeolites as epoxidation catalysts,[17] in which benzoic acid and benzaldehyde were obtained along with the major product, the styrene oxide. Obviously, we have also checked the reaction between the olefin and Oxone in the absence of copper complexes but under otherwise identical reaction conditions: no epoxide nor any other oxidation products were observed.

As mentioned above, we have already reported the immobilization of complexes **1** and **2** in silica gel as well as their use as heterogeneous catalysts for the olefin cyclopropanation reaction.[12] Now, we have found that they also catalyse the styrene oxidation, using Oxone as the oxidant, to give a mixture of styrene oxide, 1-phenylethanediol, benzaldehyde and ben-

Table 1 Epoxidation of styrene catalysed by complexes **1** and **2**

Catalyst	Styrene oxide[a]	PhCHO[a]	Yield[b] (%)
BpCu	> 85	< 5	70
Tp*Cu	> 90	< 5	60

[a] Quantified after 18 h by GC, mol% of the products. [b] Based on oxidant.

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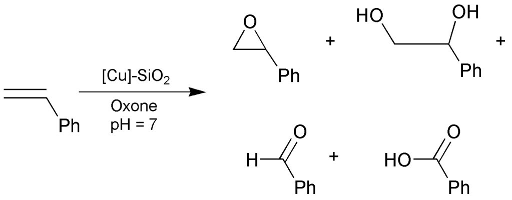
zoic acid, eqn. (2). Water is the sole solvent in this case. Table 2 displays the results of these heterogeneous experiments



(2)

(average of three cycles with the same reused catalyst). The yields, based on oxidant, are similar to those observed in the homogeneous case, although the reaction is faster in the former. The unique difference seems to be the appearance of the epoxide-opening product, the diol. This must be a consequence of the acidic nature of the solid support, the silica gel, since this transformation is usually acid-catalysed.[18] The epoxide and the diol account for 70–85% of the products (Table 2), very close to the 90% value obtained with the soluble catalysts. It is important to point out that the immobilisation of the catalyst does not seem to significantly alter the catalytic capabilities of this system, *i.e.*, it provides an excellent route to accomplish one of the permanent goals in catalysis: to heterogenise an homogeneous system without loss of the activity and/or selectivity of the latter, in order to achieve the well-known advantages of the heterogeneous system.

In conclusion, we have discovered that copper(I) complexes containing polypyrazolylborate ligands present catalytic activity towards the epoxidation reaction, as they did with the olefin cyclopropanation and aziridination reactions. These complexes can operate under both homogeneous and heterogeneous conditions, with no significant differences when moving from the former to the latter, thus achieving the well-known advantages of the recycling and reuse of the catalyst in the heterogeneous system. Moreover, the parallels between the epoxidation and the carbene and nitrene transfer reactions are reinforced since the same metal complexes assure those three catalytic conversions. Mechanistic, comparative studies for the three reactions are currently underway in this laboratory.

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Table 2 Epoxidation of styrene catalysed by complexes **1** and **2** supported on silica gel

Catalyst	Styrene oxide[a]	1-phenyl-ethanediol[a]	PhCHO[a]	PhCOOH[a]	Yield[b]
BpCu	28	38	22	11	57
Tp*Cu	17	70	3	10	68

[a] Quantified after 6 h by GC, mol% of the products. Average of three cycles.
[b] Based on oxidant.

Notes and references

† *Homogeneous catalytic experiment*: 0.05 mmol of the catalyst (**1** or **2**) was dissolved in 10 mL of acetonitrile and styrene (2 mmol) was added. An aqueous solution of Oxone (0.5 mmol, 1 mmol of $KHSO_5$, 10 mL H_2O) with three equiv. of sodium bicarbonate (1.5 mmol) was prepared and added to the catalyst-containing solution. The mixture turned greenish, and was stirred for 18 h. The products were quantified by GC, using acetophenone as an internal standard (added at the end of the reaction, immediately before quantification). The products were identified by NMR from experiments carried out in deuterated solvents, and by comparison with pure samples. The results are shown in Table 1.

Heterogeneous catalytic experiment: the copper complexes were supported as reported in ref. 12. One gram of silica-gel containing BpCu (0.02 mmol) or alternatively Tp*Cu (0.04 mmol) was suspended in 20 mL of H_2O along with 2 mmol of styrene. Neutralised Oxone (prepared as above) was added, and the mixture was stirred for 8 h. The solid was filtered off, and reused twice in an identical manner. Table 2 displays the average results of the three cycles.

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