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An unprecedented recyclable catalyst system for asymmetric hydroboration

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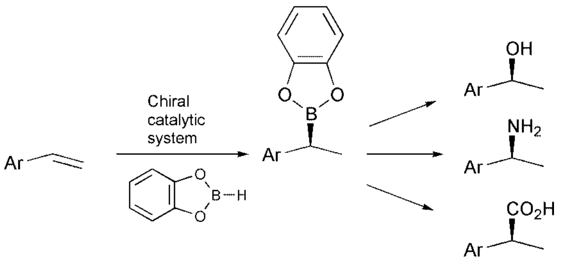
Immobilised preformed chiral homogeneous catalysts were subjected to catalytic hydroboration of styrene with catecholborane† and the activity, regio- and enantioselectivity observed were similar to those found when the corresponding homogeneous catalyst was used, remaining constant for several consecutive runs.

Recently there has been considerable interest in the heterogeneisation of chiral homogeneous catalytic systems. Many reports have shown that it is possible to design and produce new chiral catalytic systems which have obvious advantages over their soluble counterparts: they can induce asymmetry, they can be removed from the reaction mixture by simple filtration and, in many cases, they can be recycled and used again.[1]

One of the significant advantages of the optically enriched organoboron adduct (*C–B) that is derived from the catalytic asymmetric reaction of vinylarenes and catecholborane as the borane source, is that the required stereocentre can be installed. This can be followed by a consecutive *C–O,[2–4] *C–N,[5] and *C–C[6] bond-forming reaction, with stereochemical integrity (Scheme 1).

Although soluble rhodium complexes are often used to promote this reaction, the inherent problems involved in regenerating the catalytic species have yet to be resolved. In a recent attempt to address these problems, rhodium complexes modified with achiral polycyclic phosphiranes were used to perform homogeneous hydroboration–oxidation of styrene. The catalytic activity did not decrease after five consecutive catalytic runs, when styrene and catecholborane were re-added to the reaction mixture.[7] However, although the rhodium complexes were stable under O_2, the phosphiranes' ligands proved to be sensitive to alkaline H_2O_2. To prevent the catalyst from being destroyed, it has to be separated from the oxidative work-up media. These problems could be minimised to a large extent if the catalyst is separated from the reaction media before oxidation but, to the best of our knowledge this has not yet been attempted. The non-covalent immobilisation of homogeneous chiral cationic catalyst on solid supports could be an interesting alternative, because it is efficient and easy to prepare.

Here we report, for the first time, that rhodium complexes immobilised on solid supports are highly active, selective and reusable catalysts towards the hydroboration reaction of styrene.



Scheme 1

We started by examining the catalytic properties of the model rhodium complex [Rh(cod)(*R*)-(BINAP)]BF_4 **1** adsorbed on commercial montmorillonite K10, **MK10**, (BET surface area = 221 $m^2\ g^{-1}$). In the homogeneous hydroboration–oxidation of vinylarenes, the catalyst precursor **1** provides high yields and regioselectivities on 1-arylethanol derivatives but only moderate enantiomeric excesses,[2] (entry 1, Table 1). This catalytic behaviour justifies our choice of catalytic system as it reveals any increase[8,9] or decrease in the stereoselectivity induced by the supported catalyst.

Orange solutions of **1** in CH_2Cl_2 decolorised when clay was added and they were stirred for 24 h under nitrogen. The rhodium complex was believed to be mainly adsorbed on the external surface on the basis of the insignificant shift of the (001) diffraction line on the powder X-ray diffractogram between **MK10** and **1–MK10**. The amount of metal complex adsorbed by the clay (31 mg of **1** in 0.5 g of **MK10**) was determined by gravimetric analysis which measured the difference between the weights of the complex before and after immobilisation.

Once the solid-supported catalyst was prepared, it was tested for (a) activity, (b) regioselectivity, (c) enantioselectivity, (d) resistance to degradation and (e) reusability. As Table 1 shows, the activity and selectivity of catalyst **1–MK10** were lower than those of the homogeneous catalytic system under the same reaction conditions (entry 2, Table 1). The presence of significant amounts of interlamellar water in montmorillonite could favour degradation of catecholborane and/or the transition metal complex. ^{11}B NMR experiments carried out between **MK10** and catecholborane over the timescale of the catalytic experiment, showed that catecholboronic acid had formed. However when the montmorillonite was heated to at least 100 °C, **MK10T**, before the immobilization of **1**, the resulting supported catalytic system **1–MK10T** (with 40 mg of **1** in 0.5 g of **MK10T**) exhibited comparable activitiy and selectivity to the homogeneous system. Removal of the supported catalyst by filtration and repeated hydroboration recycling is demonstrated with no loss of activity or selectivity, (entry 3, Table 1).

Table 1 Asymmetric hydroboration–oxidation of styrene towards (*R*)-(+)-1-phenylethanol catalysed by the immobilised [Rh(cod)(*R*)-(BINAP)]BF_4[a]

Entry	Catalytic system	Run	Yield (%)	Branched (%)	Ee[b] (%)
1[c]	**1**	1	92	99	57
2	**1–MK10**	1	41	92	47
3	**1–MK10T**	1	96	97	55
		2	99	97	60
4	**1–Na$^+$MT**	1	26	35	5
		2	94	63	35

[a] Standard conditions: styrene–catecholborane–Rh complex = 1 : 1.1 : 0.02. Solvent: THF. *T*: 25 °C. Time: 2 h. [b] (*R*) Configuration determined by GC with chiral column FS-Cyclodex B-IP, 50 m × 0.25 mm. [c] Ref. 2 and 1 mol% precursor of catalyst.

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Remarkable difference was observed in the hydroboration of styrene when the supported catalytic system was prepared from the preheated clay bentonite **Na+MT** and the complex **1** (entry 4, Table 1). Following the same impregantion procedure, the amount of metal complex immobilised in bentonite was only 22.35 mg in 0.5 g of the clay. These data, together with the greater basal distance (from 11.8 Å in **Na+MT** to 16 Å in **1–Na+MT**), are consistent with the fact that the rhodium complexes are principally immobilised in bentonite (BET surface area = 53 $m^2\ g^{-1}$), by ion exchange and not adsorption.[8] The environment of complex **1** immobilised on the internal surface of the bentonite might be different, thus providing unexpected low conversion and selectivity on the branched product, which are improved on the second run.

The ^{19}F NMR spectra of **1** shows two singlets at δ_F −154.2 and δ_F −154.3 ppm with an intensity ratio of 1 : 4, according with the isotopic effect between ^{19}F and ^{10}B and ^{11}B respectively, Fig. 1(a), while the ^{31}P spectra show a doublet at δ_P 26.2 ppm (J_{P-Rh} = 145.4 Hz), Fig. 2(a). The intensity of these signals decreases significantly on ^{19}F and ^{31}P NMR locked spectra of a slurry in $CDCl_3$ when **MK10T** is added little by little to complex **1**. This is because **1** decreases in solution during the immobilisation process. In addition, new broad signals emerge from the baseline. Their coupling constant is identical but they are shifted to lower fields, Fig. 1 and 2.

The new signals may be broad because the montmorillonite restricts the mobility of the organometallic complex and they may shift to lower fields due to the different chemical environment provided by the solid. The fact that both nuclei (F and P) have been affected in the immobilisation process, lets us suggest that the two ionic parts of the metal complex could interact with montmorillonite through weak forces such as electrostatic and/or hydrogen bonding interactions with the surface hydroxy groups. In contrast, supported hydrogen bonded catalysts have been previously reported to take place principally in a monodentate way between the teminal silanols of different types of silica and the oxygen atom of sulfonate groups from phosphine ligands contained in the zwitterionic Rh(I) complexes[10,11] or from triflate counter-anions of cationic Ru(II)[12] and Rh(I)[11,13] complexes.

Since the recovered catalytic system **1–MK10T** could be reused with no loss of activity and selectivity, we extended the study to the cationic rhodium complex [Rh(cod)(*S*)-(QUINAP)]BF_4 **2**, modified with the P,N auxiliary ligand QUINAP {1-[2-(diphenylphosphino)-1-naphthyl]isoquinoline},[3] which provides a higher asymmetric induction than **1**.

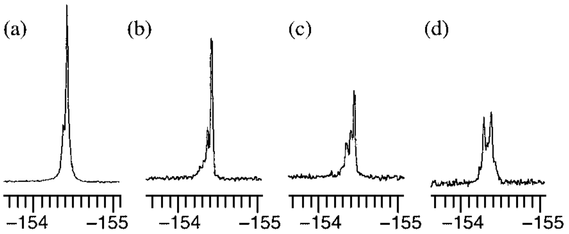

Fig. 1 ^{19}F NMR of (a) 20 mg of **1** in $CDCl_3$, (b) slurry of (a) + 50 mg of **MK10T**, (c) slurry of (b) + 50 mg of **MK10T** and (d) slurry of (c) + 25 mg of **MK10T**.

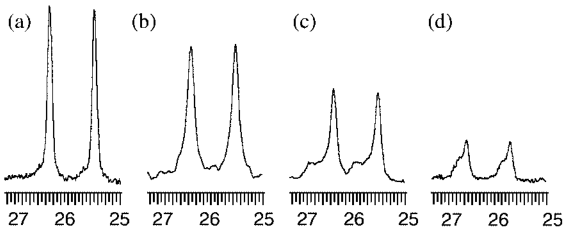

Fig. 2 ^{31}P NMR of (a) 20 mg of **1** in $CDCl_3$, (b) slurry of (a) + 50 mg of **MK10T**, (c) slurry of (b) + 50 mg of **MK10T** and (d) slurry of (c) + 25 mg of **MK10T**.

Table 2 Asymmetric hydroboration–oxidation of styrene towards (*S*)-(−)-1-phenylethanol catalysed by the immobilised [Rh(cod)(*S*)-(QUINAP)]BF_4[a]

Entry	Catalytic system	Run	Yield (%)	Branched (%)	Ee[b] (%)
1	**2**[c]	1	99	95	88
2	**2–MK10T**	1	98	97	88.5
		2	98	97	89
		3	92	97	86
		4	87	98	88

[a] Standard conditions: styrene–catecholborane–Rh complex = 1 : 1.1 : 0.02. Solvent: THF. *T*: 25 °C. Time: 1 h. [b] (*S*) Configuration determined by GC with chiral column FS-Cyclodex B-IP, 50 m × 0.25 mm. [c] Ref. 3 and 1 mol% precursor of catalyst.

We only examined four consecutive runs in the hydroboration–oxidation of styrene with **2**, (Table 2, entry 2) and in all of them the regio- and stereoselectivity were constant and comparable to the homogeneous version (Table 2, entry 1). Only the conversion decreases slightly on reuse. This was not due to leaching of the rhodium complex because no product was formed when styrene and catecholborane were added to the filtrate of the first run. The lower conversion was mainly due to the loss of solid when the catalytic system was manipulated between the runs.

The results show that the heterogeneised process is an efficient one, and further work on the characterisation of **2** tethered to montmorillonite and its applicability to the hydroboration–oxidation of other substrates such as electron-rich, electron-poor styrenes and β-substituted vinylarenes, are in progress.

Notes and references

† The IUPAC name for catecholborane is hydro[pyrocatecholato(2−)-*O*,*O′*]boran.

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