

Non-covalent immobilization of homogeneous cationic chiral rhodium–phosphine catalysts on silica surfaces†

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Non-covalent immobilization of [(*R,R*)-Me-(DuPHOS)Rh(COD)]OTf by interaction of the triflate counter ion with surface silanols of silica supports leads to an active, stable, enantioselective, asymmetric hydrogenation catalyst.

We have found that cationic rhodium complexes containing chiral bidentate phosphines can be non-covalently immobilized on silica surfaces. This method, which should be general for ionic catalysts, enables the ‘heterogenization’ of readily available enantioselective catalysts, and avoids the tedious and often difficult task of ligand modification involved in numerous previously described covalent approaches for the immobilization of homogeneous catalysts on solid supports. We demonstrate this concept through the immobilization of [(*R,R*)-Me-(DuPHOS)Rh(COD)]⁺ trifluoromethane sulfonate [Me-DuPHOS = 1,2-bis(2,5-dimethylphosphacyclopentyl)ethane] on mesoporous MCM-41 and silica gel which leads to a recyclable, non-leaching asymmetric hydrogenation catalyst with activity and selectivity equal to or greater than the homogeneous reaction. We also provide chemical and spectroscopic evidence for the mechanism of immobilization of these catalysts on silica surfaces.

The goal of heterogenization of homogeneous catalysts is to combine the superior activity and selectivity offered by homogeneous catalysts with the ease of separation and recycling of heterogeneous catalysts.^{1–3} To date, the main approach for immobilizing homogeneous catalysts on solid supports involves covalent attachment of functionalized ligands or ligand–metal complexes which typically requires multistep syntheses.^{4,5} Recently, hydrogen bonding between a sulfonated ligand and surface silanols has been demonstrated to lead to the immobilization of an achiral rhodium hydrogenation catalyst.⁶ This approach requires the sulfonation of aryl phosphines, which, while possible, also requires multistep syntheses for chiral phosphine ligands.

Our studies focused on mesoporous silica, such as MCM-41, as a solid support due to the large, tailorable and well defined pore structure, high surface area and high area density of surface silanols found in this class of silicas.^{3,7} Orange solutions of [(*R,R*)-Me-(DuPHOS)Rh(COD)]OTf **1** (OTf = trifluoromethanesulfonate, triflate) in CH₂Cl₂ rapidly decolorized upon addition of MCM-41⁹ and stirring. The powder X-ray diffraction pattern of the isolated orange powder (**2**) remains unchanged from the unfunctionalized MCM-41. Quantitative loading of the organometallic complex was demonstrated by thermal gravimetric analysis which showed 5.26% weight loss (calc. 5.29 wt%) and elemental analysis which gave 1.03 wt% Rh (calc. 0.96 wt%). The BET surface area was found to decrease from 953 m² g^{−1} in the unfunctionalized MCM-41 to 854 m² g^{−1} for composite **2** with a corresponding decrease in mesopore volume from 1.003 to 0.840 cm³ g^{−1}; this is consistent with partial mesopore filling by the organometallic catalyst.¹⁰ While this work was in progress, Augustine and Tanielyan demonstrated that cationic rhodium complexes could

be sorbed onto heteropolyacids to yield recyclable catalysts.^{11a}

³¹P and ¹⁹F NMR spectra of the free and bound complexes (**1** and **2**) suggest that it is the triflate counter ion that interacts strongly with the support in **2**. The ³¹P NMR spectrum (unlocked) of a slurry of **2** in CH₂Cl₂ shows a doublet at δ_P 76.6 (*J*_{RhP} 147 Hz) which is considerably broader [*v*_{1/2} 130 Hz, Fig. 1(b)] than that for the free complex **1** in solution [*v*_{1/2} 30 Hz, Fig. 1(a)]. The corresponding ¹⁹F NMR spectra are shown in Fig. 2. The sharp singlet (*v*_{1/2} 50 Hz) for the homogenous system [Fig. 2(a)] is broadened considerably (*v*_{1/2} 575 Hz) in the spectrum of a slurry of **2**. The line broadening seen in both the ¹⁹F and the ³¹P NMR spectra of **2** is consistent with restricted mobility of the organometallic complex within MCM-41, as would be expected for a heterogenized molecule.¹²

The counter anion is very important for the successful immobilization of the catalyst onto MCM-41. Whereas the triflate DuPhos–Rh complex **1** was effectively immobilized, the analogous complex with the lipophilic BAR_F anion {BAR_F = B[C₆H₃(CF₃)₂-3,5]₄}¹³ [(*R,R*)-Me-(DuPHOS)Rh(COD)]⁺ BAR_F[−] **3**, does not ‘load’ onto the support; solutions of **3** in CH₂Cl₂ remained orange upon addition of MCM-41. Indeed, addition of NaBAR_F to a slurry of **2** in solvent caused the solvent to take on the characteristic orange color and ³¹P NMR spectrum [*v*_{1/2} 35 Hz, Fig. 1(c)] of dissolved [(*R,R*)-Me-(DuPHOS)Rh(COD)]⁺, indicating release of the Rh cation from the support. The ¹⁹F spectrum of the triflate ion, however, remains broad and unchanged [Fig. 2(c)] indicating the triflate is still immobilized on the support. The lack of immobilization of **3** onto the support, and the lack of exchange of bound triflate for BAR_F[−] implies that triflate is strongly bound to the support and interacts with and binds the [(*R,R*)-Me-(DuPHOS)Rh(COD)]⁺ fragment to the MCM-41, a role BAR_F[−] does not fulfill.¹⁴ The mechanism of triflate binding is likely hydrogen bonding, similar to that demonstrated by Bianchini’s group in the immobilization of an achiral sulfonated phosphine–rhodium

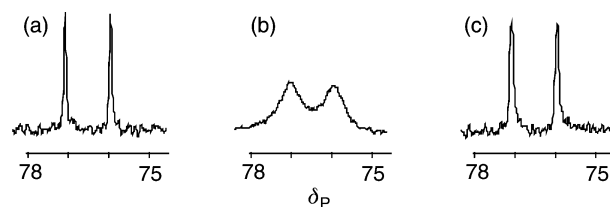


Fig. 1 ³¹P NMR of (a) **1** in CH₂Cl₂, (b) **1** after addition of MCM-41 and (c) **2** with added NaBAR_F.

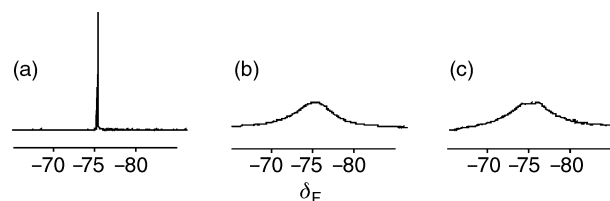


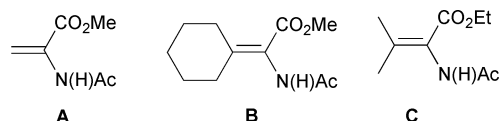
Fig. 2 ¹⁹F NMR of (a) **1** in CH₂Cl₂, (b) **1** after addition of MCM-41 and (c) **2** with added NaBAR_F.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b0/b003354p/>

Table 1 Hydrogenation results (conditions: 20 mL hexane, 8 psi H₂ and room temp. except where noted. Reaction time: **A** 30 min; **B,C**, 16 h)

Substrate	Support	Solvent	Temp	Anion	Conv. (%)	Ee (%)
A	MCM-41	Hexane	R.T.	OTf	> 99	99
A	None	Hexane	R.T.	OTf	> 99	87
A	None	MeOH	R.T.	OTf	> 99	> 99
B	MCM-41	Hexane	R.T.	OTf	> 99	98
B	None	Hexane	R.T. (50 psi)	BAr _F ^a	92	93
B	None	MeOH	R.T. (90 psi)	OTf	> 99	96.2
C	MCM-41	Hexane	R.T.	OTf	> 99	98
C	None	Hexane	R.T. (40 psi)	BAr _F ^a	26	85
C	None	MeOH	R.T. (90 psi)	OTf	99	96

^a The lipophilic BAr_F[−] anion is more soluble than OTf[−] and provided more consistent results than the OTf salt. See also ref. 13.

**Fig. 3** Substrates utilized for catalytic hydrogenation studies.

complex to silica by hydrogen bonding.⁶ Unfortunately, because of the low level of loading of the highly active catalyst (see below), we could not confirm the presence of hydrogen bonding using IR spectroscopy. Further work on other catalyst systems is underway. Other evidence that surface hydroxy groups may be involved in immobilization was found on studies of MCM-41 supports that were pretreated with trimethylsilyl chloride to protect the hydroxy groups. These supports were much less effective in immobilizing complex **1** (1.9 vs. 6.7 wt% based on Rh). We have found that other silica supports such as commercial silica gel, which are known to contain fewer surface silanols,³ also led to significantly lower loadings of **1**.

The immobilized complex **2** was found to exhibit high catalytic activity, selectivity and recoverability for the hydrogenation of three prochiral α -enamide esters, used as test substrates. Hydrogenation of enamide **A** (Fig. 3) in hexane using **2** led to complete conversion with high enantioselectivity. As shown in Table 1, the immobilized catalyst **2** led to higher activity and selectivity than the homogeneous catalyst in hexane for the β,β -disubstituted substrates **B** and **C**,¹⁵ and rivals the enantioselectivity reported in MeOH.¹⁵ For example, **B** was hydrogenated with 98% ee with **2** as the catalyst in hexane while the optimized reaction with unsupported **3** gave 96% ee in MeOH and 93% ee in hexane.¹⁵ Even more striking, the conversions for enamide **C** were significantly higher using the immobilized catalysts rather than the homogeneous analog in hexane, where conversion was only 26% (85% ee) with unsupported **3** in hexane after 22 h at 40 psi, while the reaction with **2** was complete (98% ee) after 16 h at 8 psi. Few reports¹¹ of such a positive influence on activity and selectivity for heterogenized catalysts exist. Other silica supports, including commercial silica gels, can be used to immobilize **1**; however, decreased loading (and therefore activity) was observed.

The recyclability of the immobilized catalyst was demonstrated using standard procedures. After completion of the initial hydrogenation of enamide **A**, the reaction mixture was filtered and the filtrate was tested for activity by adding more enamide; no further conversion was observed indicating the absence of highly active soluble catalyst leaching from the support. In a second set of recycling experiments, the materials were reacted under standard conditions for 30 min and the contents were then decanted leaving solid **1** in a small amount of solvent.¹⁶ The bottle was recharged, and the reaction repeated four times, with the final run differing in that the catalyst was stored in hydrogen-free hexane for 16 h prior to the final reaction. Under these conditions, the catalyst remains active with no loss of conversion or enantioselectivity.

This work clearly shows that a chiral cationic rhodium catalyst can be simply and efficiently sorbed onto silicas without any ligand modification, a method that in principle could be applied to a wide variety of cationic catalysts. The surface-bound triflate counter ion immobilizes the cationic Rh

complex onto the surface of the MCM-41 and the surface-sorbed complex is recyclable and stable to leaching from the surface in non-polar solvents. The results show that binding [(*R,R*)-Me-(DuPHOS)Rh]OTf to an MCM-41 surface has a beneficial effect on enantioselectivity and activity in the hydrogenation of prochiral enamides when compared to the homogeneous catalyst.

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