Supported BINOLate salts as base catalysts. Preparation and use in the Michael reaction

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Two silica supported BINOL complexes are prepared, both of which are active catalysts in the Michael reaction.

The use of derivatives of 1,1′-naphthalene-2,2′-diol (BINOL) as base catalysts has recently been disclosed.[1,2] In particular, the use of podand-substituted salts of BINOL has led to efficient base catalysts for the Michael reaction.[2] As part of a programme aimed at the development of heterogenised base catalysts for use in the synthesis of fine chemicals, we have prepared two BINOL derivatives supported on silica **1** and **2**, and evaluated them in the Michael reaction.

The first catalyst, **1**, was prepared from γ-aminopropylsilica[3] (AMPS, **3**) and **4**, prepared by known methods[4,5] from the commercially available poly(ethylene glycol) methacrylate (Aldrich, M_n = 306) by tosylation, displacement with the Na salt of BINOL, hydrolysis of the methacrylate, retosylation and displacement of the tosylate with **3** under reflux in toluene overnight (Fig. 1). Deprotonation of the BINOL unit was achieved by stirring with 1.5 equiv. NaOH in methanol (0.05 mol dm^{-3}) for 4 h, followed by exhaustive washing with methanol to remove excess base and physisorbed material. Thermogravimetric analysis (TGA) and elemental analysis were in agreement and indicated a loading of 0.2 mmol g^{-1}. The product was further analysed by ^{13}C–CPMAS (300 MHz, δ 8.67, 18.00, 42.93 aminopropyl; 69.57 PEG, 127.04 + weak signal at 137–140 BINOL unit). The Diffuse Reflectance FTIR (DRIFT) spectrum of the product displayed the expected peaks for the BINOL unit at 1603, 1579 and 1510 cm^{-1}.

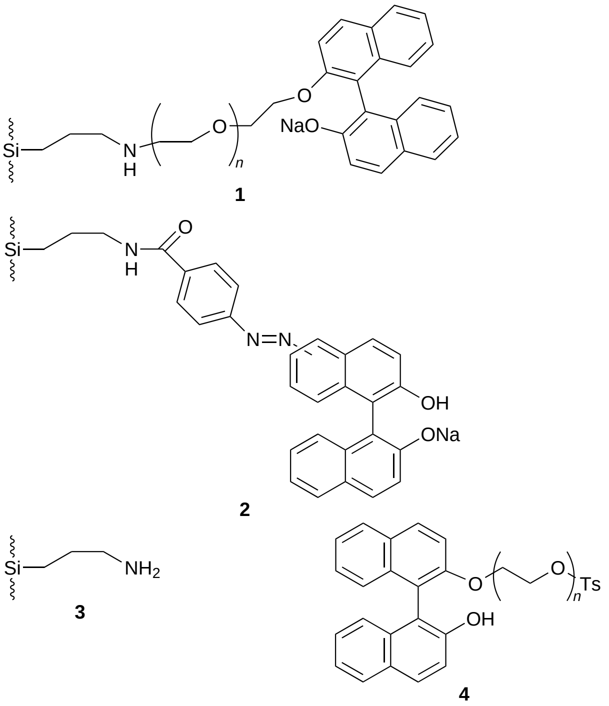
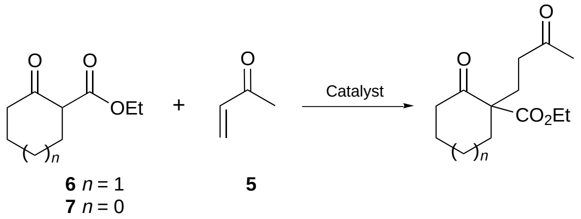


Fig. 1 structures of the silica supported catalysts and precursor

The second catalyst, **2**, was prepared, also from **3**, in four steps (amide formation with 4-aminobenzoic acid,[3] diazotisation[6] and coupling with BINOL at pH 7, followed by deprotonation). The deprotonation procedure was the same for both catalysts. Elemental analysis was consistent with the proposed catalyst structure at a loading of 0.3 mmol g^{-1}, in accordance with weight loss as measured by TGA. Diffuse reflectance UV–VIS (DRUV) spectroscopy indicated a peak at 520 nm, which corresponds well to the diazo coupling product from 4-aminobenzoic acid and BINOL after physisorption on silica. Diffuse reflectance IR spectroscopy showed peaks at 1653 and 1565 cm^{-1} (amide) and 1600, 1585 and 1506 cm^{-1} (aromatics). The position of attachment of the N=N unit to the BINOL ring system is, as yet, unknown.

The products were evaluated as catalysts in the reaction of but-3-en-2-one **5** with the β-diketones ethyl cyclohexanone 2-carboxylate **6** and ethyl 2-oxocyclopentane-2-carboxylate **7** (Scheme 1). The catalyst (0.25 g), was added to a solution of diketone (10 mmol) and but-3-en-2-one (14 mmol) in solvent (15 ml). The reaction was stirred at room temp. and monitored



Scheme 1 Michael addition between β-diketones and but-3-en-2-one, catalysed by supported BINOL catalysts

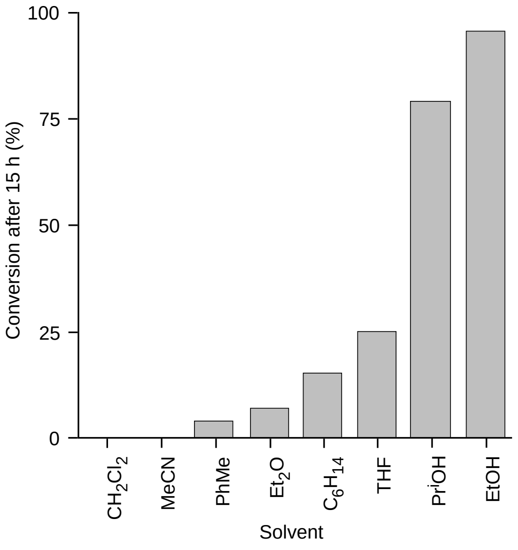


Fig. 2 Solvent dependence in the reaction between **5** and **6** at room temp. (15 ml solvent, 0.2 g dodecane as internal standard, 14 mmol **5** and 10 mmol **6**). The reaction in isopropanol was complete after 24 h.

by GC using dodecane as internal standard. The reaction of **6** using **1** as catalyst was evaluated first and displayed a remarkable solvent dependence (Fig. 2). No reaction takes place in dichloromethane or in acetonitrile, with no product being detected even after 72 h. This is remarkable since the homogeneous version of this catalyst is used in dichloromethane.[2] Toluene is poor, and ethers (diethyl ether and THF) are slightly better. The best solvents by far are alcohols, with ethanol being particularly effective, complete reaction being achieved after 15 h (Fig. 2). It is possible that the oxygen-containing solvents are better able to interact with the PEG chain, particularly the hydrogen-bonding alcohols. The relatively good performance of hexane is puzzling (we have recently observed such anomalous behaviour in different systems[7]), and it may be due to partitioning effects. Isopropanol effected complete transesterification of the product under the reaction conditions. The product can be isolated by filtration of the catalyst and normal work-up, in yields typically 5–8% lower than the GC yield. Reuse of catalyst (after decantation of the supernatant) has been studied (Table 1), and there is a gradual slowing of reaction with repeated reuse (up to four uses). Conversions are close to complete and fall off only slightly with reuse. Compound **7** reacts more rapidly under the same conditions, reaction being complete after 8 h, as opposed to 15 h with **6**. Similar slowing of reaction was observed upon reuse.‡

Table 1 Catalyst reuse in the reaction of **5** with **6** and **7**[a]

Catalyst	Substrate	Conversion (%)	*t*/h
1	**6**	97	15
1 (1 reuse)	**6**	98	16
1 (2 reuses)	**6**	99	19
1 (3 reuses)	**6**	96	23
1	**7**	99	8
2	**6**	98	28
2 (1 reuse)	**6**	98	29
2 (2 reuses)	**6**	96	28
2 (3 reuses)	**6**	97	30
2	**7**	99	15

[a] Reactions were carried out in 15 ml ethanol at room temp. with dodecane as internal standard, using 0.25 g catalyst, 10 mmol keto ester and 14 mmol enone. Isolated yields were 3–8% lower than the reported GC yields.

Compound **2** was also evaluated in the above reactions, and was found to be slightly less active [reactions took 28 h (**6**) and 15 h (**7**) respectively]. Reuse was also successful, with less reduction in performance being observed than with **1**. While a thorough solvent study has not yet been carried out on this catalyst, reaction in dichloromethane does proceed, albeit slowly, to the extent of 8% in 24 h.§

Future work will concentrate on further optimisation of the systems and extension of the methodology to other phenols, Michael reactions and to enantioselective chiral BINOL systems.

D. J. M. thanks the Royal Society for the award of a University Research Fellowship.

Footnote

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‡ Turnover numbers for **1** and **2** can thus be estimated to be of the order of 800 and 530, respectively.

§ Leaching does not appear to be a problem with either catalyst, since reactions which were interrupted before completion by removal of catalyst did not procceed after removal of the catalyst.

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Received, 10th January 1997; Com. 7/00261K