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Biomimetic Catalysis with Immobilised Organometallic Ruthenium Complexes: Substrate- and Regioselective Transfer Hydrogenation of Ketones

Kurt Polborn and Kay Severin*[a]

Abstract: Chloro-(η^6-arene) complexes of ruthenium(II) with *N*-sulfonyl-1,2-ethylenediamine ligands that have one or two styrene side chains have been synthesised and characterised. The chloro ligand was substituted with a diphenylphosphinato ligand and the resulting organometallic complexes are transition state analogues for the ruthenium-catalysed transfer hydrogenation of benzophenone. Following the protocol of molecular imprinting, these complexes were copolymerised with ethylene glycol dimethacrylate (EGDMA) in the presence of a porogen. The polymers were ground and sieved, and the phosphinato ligand was substituted with a chloro ligand, thus generating a shape-selective cavity in close proximity to the catalytically active metal centre. When tested for their ability to catalyse the reduction of benzophenone, the imprinted polymers showed a significantly higher activity (up to a factor of seven) than control polymers without cavities. Out of a mixture of seven different aromatic and aliphatic ketones, benzophenone was preferentially reduced when the imprinted polymer was used. Furthermore, the specificity of the catalyst for diaryl ketones has been confirmed in a reaction with a bifunctional substrate, 4-acetyl-benzophenone; the diaryl ketone was reduced faster with the imprinted catalyst than the acetyl group. The opposite regioselectivity was observed with the control polymer. Both the activity and the selectivity of the imprinted catalysts are dependent on how the ruthenium complexes are attached to the polymer backbone. A double connection proved to give superior results.

Keywords: catalysts · hydrogenations · molecular imprinting · ruthenium · transition states

Introduction

The activity and selectivity of metalloenzymes is determined decisively by ligands of the second coordination sphere, that is, by the microenvironment of the catalytically active centre. The implementation of a structurally defined microenvironment in synthetic organometallic catalysts would be beneficial for several applications. Due to the specific molecular recognition between substrate and catalyst, an enhanced regio, stereo, and substrate selectivity should be possible.

Two major approaches have been attempted in order to reach this goal. First, large and complex (supra)molecular systems have been synthesised, with transition metal catalysts playing an integral role.[1, 2] These systems are often based on concave organic host molecules with known binding properties, such as cyclodextrins.[2] Secondly, transition metal catalysts have been incorporated into porous macromolecular frameworks, such as zeolites, the pore size of which modulates the substrate selectivity.[3] A third and much less explored method is based on molecular imprinting (MI). MI is a technology for the introduction of specific recognition sites in highly crosslinked synthetic polymers.[4] Starting with the pioneering work of Wulff, MI has emerged as a powerful and simple tool to create "smart" polymers with most of the research being focused on analytical applications.[4] The strategy of how this technique can be employed to control the microenvironment of transition metal catalysts is outlined in Scheme 1. A catalytically active metal complex with a spectator ligand that has one or more polymerisable side chains is coordinated to a pseudosubstrate. This pseudosubstrate should be similar to the real substrate(s) in terms of size and functionality. Ideally, the resulting complex should mimic the transition state of the catalytic transformation. It is desirable to choose a pseudosubstrate with a donor group that has a sufficiently high affinity to the metal complex, since the isolation and characterisation of the transition state analogue (TSA) may then be possible. Furthermore, it ensures that the concentration of the relevant template during polymerisation is high. Following the standard protocol of MI, the TSA is subsequently co-polymerised with a large excess of a crosslinking monomer in the presence of a porogen. Selective removal of the pseudosubstrate from the resulting polymer yields an immobilised catalyst with a specific cavity in close proximity to the catalytically active metal centre.

The strategy outlined above has been used by Mosbach et al. to prepare an aldolase-mimicing synthetic polymer[5] and

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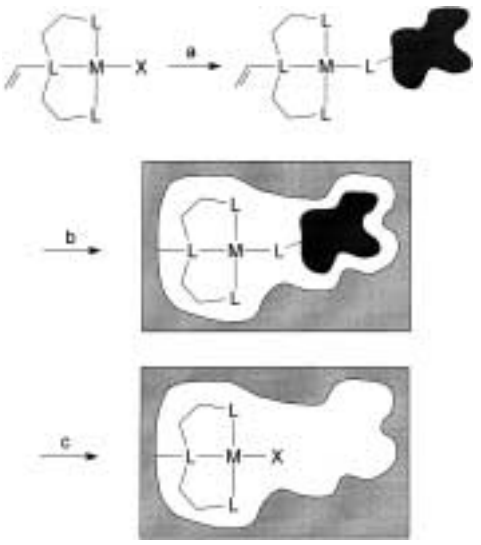
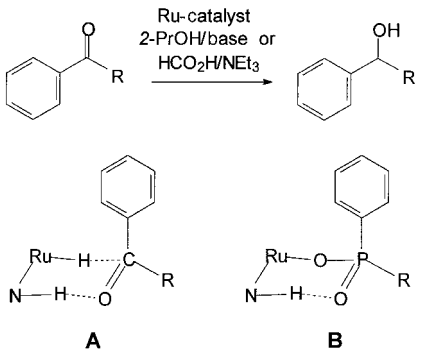


Scheme 1. Strategy to generate an immobilised catalyst with a specific cavity in close proximity to the active center: a) coordination of the catalyst to a ligand which mimics the substrate; b) polymerisation of the pseudosubstrate/catalyst complex in the presence of a porogen and a large amount of cross-linker; c) selective removal of the pseudo-substrate.

by Lemaire et al. to produce a catalytically active polymer for the asymmetric reduction of ketones.[6] Both groups utilised classical coordination compounds, a Co^{II} pyridine complex or a Rh^{I} amine complex, respectively, which were prepared in situ prior to polymerisation and were not further characterised. Preliminary studies about molecular imprinting with titanium catalysts have been presented by the group of Gagné.[7]

The transfer hydrogenation of ketones catalysed by half-sandwich complexes of ruthenium(II) has recently received much attention, because highly active and enantioselective catalysts can be obtained when certain amine-based ligands are used.[8] For reactions of this kind, a six-membered cyclic transition structure, **A**, was proposed by Noyori (Scheme 2).[8b] Computational studies have recently provided additional



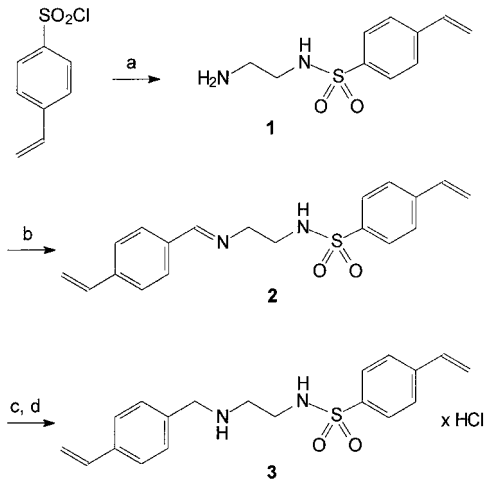
Scheme 2. **A**: the proposed transition structure for the transfer hydrogenation of aromatic ketones catalysed by (η^6-arene)Ru^{II} complexes; **B**: phosphinato complexes as transition state analogues. R = alkyl, aryl.

evidence for such a geometry.[9] We suggested phosphinato complexes of the general formula **B** to imitate this structure with a pseudosubstrate ruthenium complex.

In a preliminary communication, we reported the synthesis and molecular structure of an organometallic TSA (**7**) for the transfer hydrogenation of benzophenone.[10] To best of our knowledge, this (η^6-arene)Ru^{II} complex, with a diphenylphosphinato ligand that acts as a pseudosubstrate, represents the first isolated and structurally characterised organometallic TSA. The complex was incorporated into a synthetic organic polymer following the imprinting protocol. The resulting catalyst was shown to be three times more active than a control polymer prepared with a complex without pseudosubstrate (**4**) and was specific for benzophenone.[10] A similar methodology was used to generate an immobilised chiral rhodium(III) complex, which catalyses the asymmetric reduction of aromatic ketones with high enantiomeric excess.[11] We herein report on the synthesis and spectroscopic properties of the above-mentioned ruthenium complexes and the corresponding ligands. Furthermore, second-generation catalysts are described that have two styrene side chains (**6**, **8**). Even higher rate enhancements (factor of seven) were observed with these catalysts. To demonstrate the specificity of the imprinted catalyst for benzophenone, a competition experiment with six different cosubstrates was performed. The regioselectivity of the catalysts was addressed in a reaction with the bifunctional substrate, 4-acetylbenzophenone.

Results and Discussion

Synthesis of the ruthenium complexes: The synthesis of the ligands employed in this study is outlined in Scheme 3. Treatment of ethylene diamine with 4-vinyl-benzenesulfonyl



Scheme 3. a) $H_2NCH_2CH_2NH_2$, CH_2Cl_2; b) 4-vinylbenzaldehyde, 4 Å, CH_2Cl_2; c) $NaBH_4$, MeOH; d) HCl/Et_2O.

chloride gives monosubstituted ligand **1**. The introduction of a second styrene group is achieved by condensation of **1** with 4-vinylbenzaldehyde. Since the presence of NH moieties was shown to be crucial for successful catalytic transformations,[8b] imine **2** was subsequently reduced with $NaBH_4$ to give disubstituted ligand **3**.

A racemic mixture of ruthenium complexes **4** and **5** was prepared by treating [{(η^6-arene)$RuCl_2$}$_2$] (arene = *p*-cymene,

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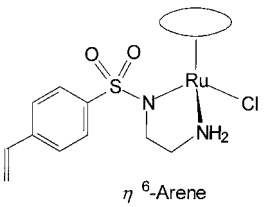


	η^6-Arene
4	*p*-Cymene
5	C_6Me_6

C_6Me_6) with the sodium salt of amine ligand **1**. Both complexes are chiral, with the ruthenium atom as the stereogenic centre and a ligand that acts as an anionic *N*,*N*′-chelate.

The ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature shows a broad signal at $\delta = 1.2$ for the diasterotopic methyl groups of the cymene ligand and a series of broad signals between $\delta = 5$ and 6 for the diasterotopic CH protons of the cymene ligand. These signals sharpen to some extent upon heating the sample to 55 °C. The underlying dynamic process is the epimerisation of the chiral metal centre. When the spectrum is recorded in a mixture of $CDCl_3$ and CD_3OD, this process is fast relative to the NMR timescale and a well-resolved spectrum is obtained. This is in accordance with other studies of chiral ruthenium half-sandwich complexes, which have shown that the rate of epimerisation strongly depends on the polarity of the solvent.[12] Interestingly, compounds **4** and **5** are both soluble in water. It is most likely that the chloro ligand in this medium is replaced by a water molecule to form a cationic solvato complex as was suggested for other Ru^{II} half-sandwich complexes.[13] Unfortunately, complex **5** has a poor solubility in organic solvents, such as dichloromethane and chloroform, and therefore was not used for molecular imprinting studies.

The structure of one enantiomer of **5** in the crystal state is shown in Figure 1. The geometry around the ruthenium atom can be described as pseudo-octahedral and the η^6-arene ring

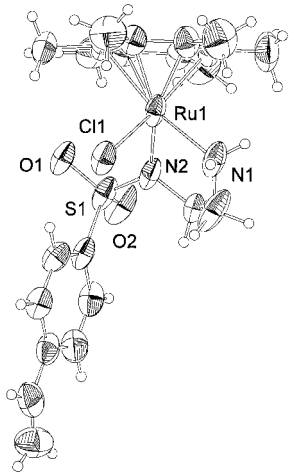
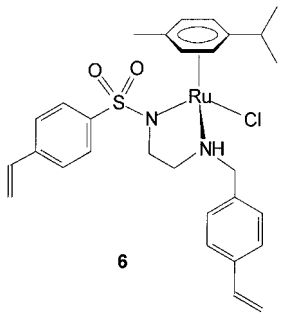


Figure 1. Molecular structure of **5** in the crystal. Selected bond lengths [pm] and angles [°]: Ru1–N1 212.7(6), Ru1–N2 213.1(8), Ru1–Cl1 241.7(2), S1–N2 157.7(7); N1-Ru1-N2 78.0(3), N1-Ru1-Cl1 83.6(2), N2-Ru1-Cl1 89.3(2).

and other ligands form a "piano stool" configuration. Due to the restraints of the *N*,*N*′-chelate, the N1-Ru-N2 angle (78.0°) is smaller than the N1-Ru-Cl (83.6°) and the N2-Ru-Cl angles (89.3°). The Ru–Cl and Ru–N bond lengths are comparable to those found in related ruthenium complexes.[14]

Similarly to **4** and **5**, the ruthenium complex **6** was obtained by reaction of $[\{(p\text{-cymene})RuCl_2\}_2]$ with the anion of amine ligand **3**. The complex has two stereogenic centres, the amine



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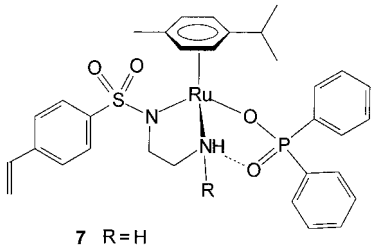
nitrogen atom and the metal atom, and the formation of two diastereoisomers was thus expected. The ^{1}H NMR spectrum of **6** ($CDCl_3$, 55 °C), however, shows only one set of signals. Below that temperature, broad signals point to dynamic processes. These results suggest that epimerisation of one of the stereogenic centres is fast on the NMR timescale, which is in agreement with the results obtained for **8** (see discussion below).



7 R = H
8 R = $CH_2C_6H_4CH{=}CH_2$

The chloro ligand in **4** and **6** can be substituted with a diphenylphosphinato ligand (the pseudosubstrate) with the use of the silver salt of diphenylphosphinic acid. No reaction was observed with the sodium salt. In perfect agreement with the postulated transition structure (Scheme 2), the phosphinato ligand in **7** acts as a monodentate ligand with an additional hydrogen bond to the adjacent amine group. This was established by the result of a single-crystal analysis of **7**.[10] A similar geometry is assumed for complex **8**. As for compound **6**, only one set of signals is observed for complex **8** although two stereogenic centres are present ($CDCl_3$, 23 °C). At temperatures below −50 °C, however, two isomers can be detected by ^{31}P NMR spectroscopy, the relative ratio of which is 8:1 (Figure 2). These results show that the formation of **8** is highly diastereoselective and that epimerisation processes occur within the NMR timescale.

Preparation of the polymeric catalysts: The complexes **4** and **6**–**8** were copolymerised with ethylene glycol dimethacrylate (Ru:EGDMA = 1:99) in the presence of $CHCl_3$, a solvent which acts as a porogen and helps to dissolve the ruthenium complexes. The combination of EGDMA and $CHCl_3$ has

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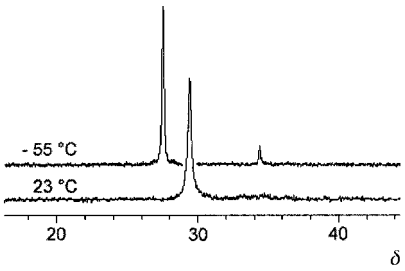
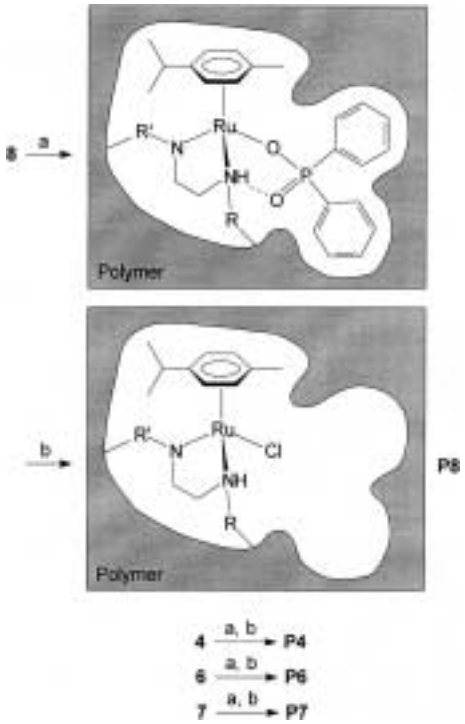


Figure 2. ^{31}P NMR spectrum of **8** at 23 and $-55\,^{\circ}C$ ($CDCl_3$).

previously been shown to be well suited for imprinting studies.[15] To initiate the reaction, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) was employed. In contrast to 2,2′-azobisisobutyronitrile (AIBN), the thermal initiator normally used in molecular imprinting, V-70 allows the polymerisation to be carried out under mild conditions (35 °C) and thus the incorporation of sensitive organometallic complexes is possible.

After polymerisation, the orange polymers were ground and sieved to obtain uniform particle sizes (25–100 μm). The polymers were then treated with a solution of $[BnNEt_3]Cl$ in methanol. During this procedure, the phosphinato ligands are removed and replaced by chloro ligands, thereby generating a form-selective cavity (Scheme 4).[16] Elemental analyses with



Scheme 4. Immobilisation of ruthenium complexes. a) EGDMA, $CHCl_3$, V-70, 35 °C, 20 h, then 65 °C, 4 h; b) $[BnNEt_3]Cl$ in MeOH (0.1M).

ICP-AES have indicated that at least 80 % of the template is released by this procedure (Table 1). Polymers **P4** and **P6**–**P8** were then washed extensively with methanol and dried in vacuo. It is important to note that the imprinted catalyst **P8** and the control catalyst **P6** have the same chemical composition (Table 1). The only difference is the microenvironment of the ruthenium complexes. The same is true for **P7** and **P4**.

Table 1. Elemental analyses of the polymers.

Polymer	C [%]	H [%]	Ru [%][a]	P[%][a]
P4	59.60	7.23	0.41	–
P6	59.78	7.13	0.41	–
P7	59.59	7.15	0.37	≤ 0.02
P8	59.73	7.13	0.37	≤ 0.02
EGDMA $\cdot 0.17 H_2O \cdot 0.77 \times 10^{-2}$ **8** (calcd)	59.75	7.14	0.37	0.11

[a] Determined with ICE-AES.

Transfer hydrogenation: Transfer hydrogenations of aromatic ketones with (η^6-arene)Ru^{II} complexes that contain *N*-sulfonyl-1,2-ethylenediamine ligands can be performed with 2-propanol or formic acid as the reducing agent.[8] With the latter hydrogen donor, the reaction is quasi-irreversible (generation of CO_2) and 100 % conversion can be achieved in theory. Furthermore, the reactions can be performed in air without the need for an inert atmosphere. When tested for their ability to catalyse the reduction of benzophenone with azeotropic HCO_2H/NEt_3,[17] all polymers (**P4**, **P6**–**P8**) displayed a high activity: with 1 mol % catalyst at 70 °C, initial turnover frequencies (TOF) of more than $10\,h^{-1}$ were determined. This indicates good incorporation[18] and accessibility of the ruthenium complexes in the porous organic matrix. Quantification of the catalytic activity revealed that the imprinted polymers were significantly more active than the control polymers: for **P7** and **P4**, a difference in the initial rates of a factor of three was observed.[10] Under identical conditions, the difference in activity between **P8** and **P6** was even higher (more than a factor of five, Figure 3). This rate

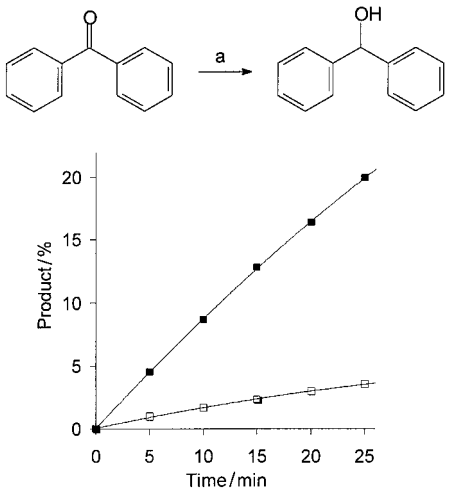


Figure 3. Product formation as a function of time for the transfer hydrogenation of benzophenone in the presence of catalyst **P8** (■) or **P6** (□). The data represent averaged values from two independent experiments; the errors are less than 0.4 %. a) azeotropic HCO_2H/NEt_3, CH_3CN, Ru catalyst, 70 °C (benzophenone:Ru = 100:1).

enhancement is remarkable considering the fact that the imprinted and the control polymer contain the same amount of ruthenium complexes.

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The improved relative performance of imprinted catalyst **P8** is most likely the result of the reduced flexibility of the second-generation ruthenium complexes within the polymeric matrix. Since they are connected by two styrene side chains to the polymer backbone, the catalytically active metal centre is fixed and thus more precisely positioned opposite to the cavity.

With the new polymers **P8** and **P6**, we also carried out the reduction of benzophenone with the use of 2-propanol as the reducing agent. Both the observed rate enhancement (factor of 6.5) as well as the absolute rates are slightly higher than with formic acid.

The form-selective cavity obtained by molecular imprinting is not only expected to affect the activity, but also the substrate selectivity of the catalyst. Indeed, competition experiments with equal amounts of benzophenone and a second ketone with the polymeric catalysts **P7** and **P4** have shown that molecular imprinting with a diphenylphosphinato ligand enhances the specificity for benzophenone.[10] We performed a more complicated experiment with the second-generation catalysts. Equal amounts of seven different ketones (**S1**–**S7**), one of which was benzophenone, were reduced in the presence of imprinted polymer **P8** or control polymer **P6**. The product distribution after 20 minutes is shown in Figure 4. With the control catalyst **P6** only low conversion with no significant preference for either substrate was observed. The imprinted catalyst **P8**, on the other hand, was not only significantly more active, but also specific for benzophenone: diphenylmethanol is clearly the dominant product in the reaction mixture. The relative increase in yields for all substrates are quite informative (Figure 4). A factor of 6.6 is observed for benzophenone. The value drops to 3.1 or 3.2 for the aromatic ketones, tetralone and acetophenone, respectively. This shows that the catalyst can differentiate between structurally very similar substrates, such as acetophenone and benzophenone. As expected, for reactions with aliphatic substrates like 2-adamantanone, a relatively low increase in yield is observed (factor of 2.1).

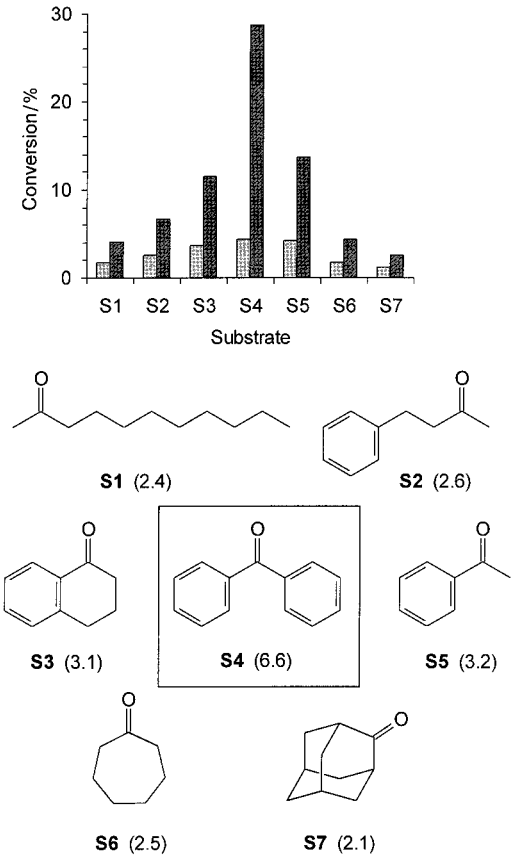
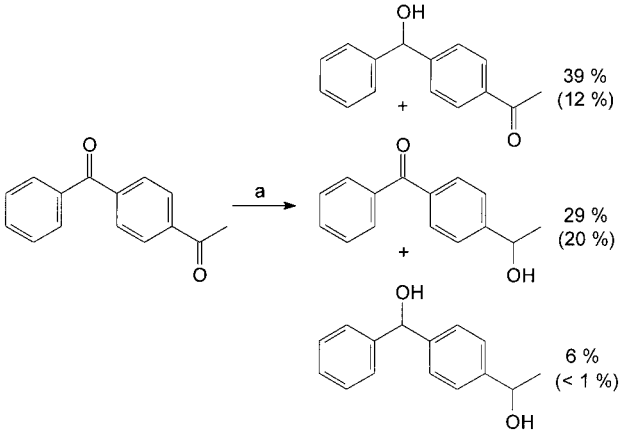


Figure 4. Transfer hydrogenation of a mixture of seven different ketones (**S1**–**S7**) in the presence of catalyst **P8** or **P6**. Product distribution after 20 min reveals that the MIP catalyst **P8** (dark grey) is significantly more active than the control catalyst **P6** (light grey). Furthermore, **P8** shows a pronounced selectivity for benzophenone. The values for the relative increase in yields are reported below.

We were also interested whether imprinted catalyst **P8** would preferentially reduce a diarylketo group within a multifunctional substrate. To address this question, we synthesised 4-acetylbenzophenone. This molecule contains both a diaryl-keto and an acetyl group. The results obtained with this substrate and the MIP catalyst **P8** or the control catalyst **P6** with formic acid as the reducing agent are summarised in Scheme 5. After one hour, 33% of the substrate was reduced when control catalyst **P6** was used. The product distribution reveals that the sterically less crowded acetyl group was reduced almost twice as fast as the diarylketo group. Again, the MIP catalyst **P8** was more active: after one hour, 74% of 4-acetylbenzophenone had reacted under identical conditions. More importantly, the selectivity was reversed; the dominant product was now diarylmethanol (Scheme 5). These results show that the regioselectivity can also be controlled when a TSA is used in combination with molecular imprinting.[19] The difference in selectivity in this experiment would probably have been even higher, if the correct pseudosubstrate, that is, (4-acetylphenyl)phenylphosphinate, had been used as a template.



Scheme 5. Transfer hydrogenation of 4-acetylbenzophenone in the presence of catalyst **P8** and **P6**. a) azeotropic HCO_2H/NEt_3, CH_3CN, 70 °C. The product distribution after 1 h is reported (the values in brackets correspond to the reaction with catalyst **P6**).

Conclusion

We have shown that structurally defined organometallic transition state analogues in combination with an imprinting technique can be used to generate immobilised catalysts with

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a shape-selective cavity in close proximity to the catalytically active centre. As a result, these catalysts show a significantly enhanced activity. Furthermore, they are specific and, thus, substrate- and regio-selective transformations can be performed. Both the activity and the selectivity are dependent on how the metal complexes are attached to the polymer backbone: a rigid connection by two styrene side chains was shown to be superior.

The manipulation of the microenvironment of organometallic complexes often requires an elaborate molecular design. In our approach, specific cavities are formed by self-assembly of small molecules around an organometallic TSA with subsequent covalent capture.[20] The advantage of this method is its generality and simplicity. We are currently applying this technique to other transition metal-catalysed reactions.

Experimental Section

General: The synthesis of all ruthenium complexes as well as the transfer hydrogenation with 2-propanol was performed under an atmosphere of dry dinitrogen and by using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and stored under dinitrogen prior to usage. EGDMA was washed with NaOH (1M) and saturated NaCl solution and dried with Na_2SO_4. After filtration, the monomer was distilled under reduced pressure. The azo initiator V-70 was a gift from Wako Chemicals. 4-Acetylbenzophenone was prepared by oxidation of commercially available 4-ethylbenzophenone with $KMnO_4/CuSO_4 \cdot (H_2O)_n$ (CH_2Cl_2, 350 h) and recrystallised from hot hexane. 4-Vinylbenzenesulfonyl chloride,[21] 4-vinylbenzaldehyde,[22] $[\{(p\text{-cymene})RuCl_2\}_2]$[23] and $[\{(C_6Me_6)RuCl_2\}_2]$[23] were prepared according to literature procedures. The ^1H; ^{13}C and ^{31}P NMR spectra were recorded on a JEOL EX 400 or a GSX 270 spectrometer. All spectra were recorded at room temperature unless stated otherwise. The GC analysis was performed with a Varian 3800 spectrometer with a CP-Cyclodextrin-B-2,3,6-M-19 column (50 m).

$H_2NCH_2CH_2NHSO_2C_8H_7$ (1): A solution of 4-vinylbenzenesulfonyl chloride (5 mL) in dichloromethane (15 mL) was slowly added (1 h) to a solution of ethane-1,2-diamine (5 mL) in dichloromethane (10 mL). The yellow suspension was stirred for 2 h, then dichloromethane (200 mL), H_2O (100 mL) and HCl/H_2O (2M, 200 mL) were added. After separation of the layers, the water phase was washed twice with dichloromethane, filtered and then neutralised with KOH (2M, pH 9–10). The mixture was extracted with dichloromethane (3 × 150 mL). After drying over Na_2SO_4, filtration and evaporation of the solvent, a slightly yellow powder was obtained (3.8 g). Yield: 68%; m.p. 127–128°C; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 2.17 (br m, 2H; NH_2), 2.80 (m, 2H; CH_2), 2.97 (m, 2H; CH_2), 5.42 (d, $^3J =$ 11 Hz, 1H;; CH=CH_2), 5.87 (d, $^3J = 17$ Hz, 1H; CH=CH_2), 6.75 (dd, $^3J =$ 11, 17 Hz, 2H; CH=CH_2), 7.52 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.81 (d, $^3J = 8$ Hz, 2H; C_6H_4); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 40.89$, 45.15 (CH_2), 116.30, 126.52, 127.05, 135.38, 139.31, 141.88 (C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{10}H_{14}N_2O_2S \cdot 0.25\,H_2O$ (230.80): C 52.04, H 6.33, N 12.14; found C 52.34, H 6.30, N 12.12.

$C_8H_7CH=NCH_2CH_2NHSO_2C_8H_7$ (2): A solution of **1** (1.0 g, 4.42 mmol) and 4-vinylbenzaldehyde (584 μL, 4.42 mmol) in dichloromethane (30 mL) was stirred at room temperature in the presence of molecular sieves (4 Å). After 24 h, the solids were removed by filtration. The solvent was evaporated in vacuo and the remaining oil was stirred in diethyl ether (60 mL) to give a white precipitate (590 mg). A second fraction of analytically clean product was obtained by cooling the mother liquor to −20°C (330 mg). Yield: 61%; m.p. 101–103°C; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 3.30–3.31 (m, 2H; CH_2), 3.64 (t, $^3J = 6$ Hz, 2H; CH_2), 5.30 (m, 1H; NH), 5.32 (d, $^3J = 11$ Hz, 1H; CH=CH_2), 5.40 (d, $^3J = 11$ Hz, 1H; CH=CH_2), 5.81 (d, $^3J = 18$ Hz, 1H; CH=CH_2), 5.84 (d, $^3J = 18$ Hz, 1H; CH=CH_2), 6.71 (dd, $^3J = 11$, 18 Hz, 2H; CH=CH_2), 7.40 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.45 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.57 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.79 (d, $^3J = 8$ Hz, 2H; C_6H_4), 8.12 (s, 1H; CH=N); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta =$ 43.90, 60.04 (CH_2), 115.59, 117.37, 126.53, 126.81, 127.48, 128.56, 135.03, 135.45, 136.28, 139.03, 140.29, 141.81 (C_6H_4–CH=CH_2), 163.15 (CH=N); elemental analysis calcd (%) for $C_{19}H_{20}N_2O_2S$ (340.44): C 67.03, H 5.92, N 8.23; found C 67.15, H 5.87, N 8.23.

$[C_8H_7CH_2NH_2CH_2CH_2NHSO_2C_8H_7]Cl$ (3): $NaBH_4$ (50 mg, 1.32 mmol) was added to a solution of **2** (400 mg, 1.18 mmol) in methanol (10 mL). After stirring for 15 min at room temperature, the solution was heated under reflux for another 15 min. The solvent was removed in vacuo. The residue was extracted with diethyl ether (100 mL), washed three times with water and dried over Na_2SO_4. After evaporation of the solvent, the product was redissolved in diethyl ether (40 mL) and precipitated as the HCl adduct with a few milliliters of HCl-saturated ethyl acetate to give a white powder (380 mg). Yield: 61%; m.p. 181–183°C; ^1H NMR (270 MHz, $CDCl_3$): $\delta =$ 2.65–2.69 (m, 2H; CH_2), 2.98–3.02 (m, 2H; CH_2), 3.62 (s, 2H; CH_2), 5.23 (dd, $^2J = 0.8$ Hz, $^3J = 10.9$ Hz, 1H; CH=CH_2), 5.41 (d, $^3J =$ 10.9 Hz, 1H; CH=CH_2), 5.72 (d, $^2J = 0.8$ Hz, $^3J = 17.4$ Hz, 1H; CH=CH_2), 5.85 (d, $^3J = 17.6$ Hz, 1H; CH=CH_2), 6.64–6.77 (m, 2H; CH=CH_2), 7.15 (d, $^3J = 8.2$ Hz, 2H; C_6H_4), 7.32 (d, $^3J = 8.3$ Hz, 2H; C_6H_4), 7.47 (d, $^3J = 8.6$ Hz, 2H; C_6H_4), 7.79 (d, $^3J = 8.4$ Hz, 2H; C_6H_4); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta =$ 42.51, 47.51, 52.93 (CH_2), 113.76, 117.38, 126.39, 126.81, 127.47, 128.34, 135.45, 136.57, 138.72, 139.45, 141.77 (C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{19}H_{23}ClN_2O_2S$ (378.91): C 60.23, H 6.12, N 7.39; found C 59.21, H 6.10, N 7.15.

[(*p*-Cymene)Ru{$NH_2CH_2CH_2NSO_2C_8H_7$}Cl] (4): A solution of NaOMe (1.0 mmol) in methanol (2M) was added to a solution of **1** (226 mg, 1.0 mmol) in dichloromethane/methanol (1:1; 15 mL). The resulting solution was slowly added (15 min) to a solution of $[\{(p\text{-cymene})RuCl_2\}_2]$ (306 mg, 0.5 mmol) in dichloromethane (20 mL). After 3 h, the solvent was removed in vacuo. The residue was stirred with dichloromethane/diethyl ether (2:1; 30 mL). After filtration, the solution was reduced to a volume of 2 mL in vacuo. Addition of hexane (15 mL), evaporation of the solvent and drying in vacuo yielded an orange powder (457 mg). Yield: 89%; m.p. 192–194°C; ^1H NMR (400 MHz, $CDCl_3/CD_3OD$, 4:1, 55°C): $\delta = 1.11$ (d, $^3J =$ 7 Hz, 6H; $CH(CH_3)_2$), 2.01 (s, 3H; CH_3, cymene), 2.10 (br m, 4H; NCH_2), 2.68 (sept, $^3J = 7$ Hz, 1H; CH(CH_3)$_2$), 5.15 (d, $^3J = 11$ Hz, 1H; CH=CH_2), 5.33 (br d, $^3J = 5$ Hz, 2H; CH, cymene), 5.48 (d, $^3J = 5$ Hz, 2H; CH, cymene), 5.64 (d, $^3J = 18$ Hz, 1H; CH=CH_2), 6.55 (dd, $^3J = 11$, 18 Hz, 1H; CH=CH_2), 7.26 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.67 (d, $^3J = 8$ Hz, 2H; C_6H_4); ^{13}C NMR (101 MHz, $CDCl_3/CD_3OD$, 4:1, 50°C): $\delta = 18.31$, 22.17 (CH_3, cymene), 30.54 (CH, cymene), 46.86, 48.52 (NCH_2), 81.50 (br, CH, cymene), 96.40, 102.20 (C, cymene), 115.31, 125.82, 127.49, 135.99, 139.61, 142.17 (C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{20}H_{27}ClN_2O_4RuS \cdot H_2O$ (514.04): C 46.73, H 5.69, N 5.45; found C 47.03, H 5.36, N 5.32.

[(C_6Me_6)Ru{$NH_2CH_2CH_2NSO_2C_8H_7$}Cl] (5): The synthesis of **5** was performed analogous to that of **4.** Dichloromethane/diethyl ether (6:1, 90 mL) was used to extract the product. Yield: 78%; orange powder; m.p. 159–162°C; ^1H NMR (400 MHz, $CDCl_3/CD_3OD$, 4:1): $\delta = 1.96$ (s, 6H; CH_3), 1.99 (t, $^3J = 5$ Hz, 2H; NCH_2), 2.25 (t, $^3J = 5$ Hz, 2H; NCH_2), 5.09 (d, $^3J = 11$ Hz, 1H; CH=CH_2), 5.58 (d, $^3J = 18$ Hz, 1H; CH=CH_2), 6.49 (dd, $^3J = 11$, 18 Hz, 1H; CH=CH_2), 7.17 (d, $^3J = 8$ Hz, 2H; C_6H_4), 7.68 (d, $^3J =$ 8 Hz, 2H; C_6H_4); ^{13}C NMR (101 MHz, $CDCl_3/CD_3OD$, 4:1): $\delta = 15.72$ (CH_3), 44.86, 49.38 (NCH_2), 91.10 (C_6Me_6) 115.20, 125.64, 128.07, 135.89, 139.31, 142.56 (C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{22}H_{31}ClN_2O_4RuS \cdot 0.25\,CH_2Cl_2$ (545.32): C 49.01, H 5.82, N 5.14; found C 48.95, H 5.99, N 5.05.

[(*p*-Cymene)Ru{$NH(CH_2C_8H_7)CH_2CH_2NSO_2C_8H_7$}Cl] (6): A solution of NaOMe (2.0 mmol) in methanol (2M) was added to a suspension of **3** (378 mg, 1.0 mmol) in dichloromethane (10 mL). The resulting solution was slowly added (15 min) to a solution of $[\{(p\text{-cymene})RuCl_2\}_2]$ (306 mg, 0.5 mmol) in dichloromethane (10 mL). After 15 h, the mixture was filtered and the solvent removed in vacuo. The product was purified by flash chromatography (chloroform/methanol 9:1, silica gel) and crystallised by slow diffusion of hexane into a solution of **6** in dichloromethane. Yield: 68%; m.p. 203–205°C (decomp); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.30$ (d, $^3J = 7$ Hz, 3H; $CH(CH_3)_2$), 1.34 (d, $^3J = 7$ Hz, 3H; $CH(CH_3)_2$), 2.11–2.45 (m, 3H; CH_2), 2.22 (s, 3H; CH_3, cymene), 2.94–3.07 (m, 2H; CH_2, CH(CH_3)$_2$), 3.82 (br s, NH), 4.13 (dd, $^2J = 13$ Hz, $^3J = 10$ Hz, 1H; NCH_2Ar), 4.25 (dd, $^2J = 13$ Hz, $^3J = 4$ Hz, 1H; NCH_2Ar), 5.23–5.82 (m, 8H; CH-cymene, CH=CH_2), 6.62–6.74 (m, 2H; CH=CH_2), 7.24–7.43 (m, 6H; C_6H_4), 7.78 (d, $^3J = 8$ Hz, 2H; C_6H_4); ^{13}C NMR (68 MHz, CD_3OD): $\delta =$ 18.96, 21.94, 23.03 (CH_3), 30.97 (CH(CH_3)$_2$), 48.25, 54.93, 61.15 (CH_2),

79.60, 79.92, 82.67, 83.46 (CH, cymene), 96.49, 102.60 (C, cymene), 114.97, 125.73, 126.96, 128.01, 128.64, 135.31, 136.02, 136.45, 138.24, 139.46, 142.46 (C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{29}H_{35}ClN_2O_2RuS$ (612.19): C 56.90, H 5.76, N 4.58; found C 56.55, H 5.77, N 4.37.

[(*p*-Cymene)Ru{$NH_2CH_2CH_2NSO_2C_8H_7$}(O_2PPh_2)] (7): A suspension of **4** (103 mg, 0.20 mmol) and [AgO_2PPh_2] (72 mg, 0.22 mmol) in dichloromethane (10 mL) was stirred for 72 h in the dark. After filtration, the solvent was reduced to 2 mL in vacuo. Addition of hexane (15 mL), evaporation of the solvent and drying in vacuo gave 128 mg of an orange powder. Yield: 91 %; m.p. 190–192 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$/CD_3OD, 4:1, 55 °C): $\delta = 1.00$ (d, $^3J = 7$ Hz, 6H; CH(CH_3)$_2$), 1.67 (s, 3H; CH_3, cymene), 2.07–2.09 (m, 2H; NCH_2), 2.26 (sept, $^3J = 7$ Hz, CH(CH_3)$_2$), 2.29–2.36 (m, 2H; NCH_2), 5.20 (d, $^3J = 11$ Hz, 1H; CH=CH_2), 5.29 (br m, 2H; CH, cymene), 5.39–5.41 (br m, 2H; CH, cymene), 5.66 (d, $^3J = 18$ Hz, 1H; CH=CH_2), 6.60 (dd, $^3J = 11$, 18 Hz, 1H; CH=CH_2), 7.13–7.42 (m, 12H; C_6H_4, C_6H_5), 7.73 (d, $^3J = 6$ Hz, 2H; C_6H_4); ^{13}C NMR (68 MHz, $CDCl_3$/CD_3OD, 4:1, 55 °C): $\delta = 17.57$, 21.90 (CH_3, cymene), 30.16 (CH, cymene), 45.77, 48.96 (NCH_2), 79.81, 81.38 (CH, cymene), 95.14, 100.47 (C, cymene), 115.44, 125.99, 127.09, 127.71, 127.90, 130.33, 130.92, 131.06, 135.89, 136.69, 138.66, 139.85, 143.40 (C_6H_4–CH=CH_2, Ph); ^{31}P NMR (109 MHz, $CDCl_3$/CD_3OD, 4:1, 109 MHz): $\delta = 30.17$; elemental analysis calcd (%) for $C_{32}H_{37}N_2O_4PRuS \cdot 0.33\,CH_2Cl_2$ (706.07): C 55.00, H 5.38, N 3.97; found C 55.37, H 5.74, N 4.02.

[(*p*-Cymene)Ru{$NH(CH_2C_8H_7)CH_2CH_2NSO_2C_8H_7$}($O_2PPh_2$)] (8): The synthesis was performed analogous to that of **7**. Yield: 87 %; orange powder; m.p. 146–150 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.18$ (d, $^3J = 7$ Hz, 3H; CH(CH_3)$_2$), 1.24 (d, $^3J = 7$ Hz, 3H; CH(CH_3)$_2$), 1.27 (m, 2H; CH_2), 1.78 (s, 3H; CH_3, cymene), 1.81–1.99 (m, 1H; CH_2), 2.09–2.14 (m, 1H; CH_2), 2.56 (m, 1H; CH(CH_3)$_2$), 2.96–3.02 (m, 1H; CH_2), 3.96–4.05 (m, 1H; CH_2), 5.24–5.92 (m, 8H; CH-cymene, CH=CH_2), 6.63–6.78 (m, 2H; CH=CH_2), 7.20–7.57 (m, 16H; C_6H_4), 7.87(d, $^3J = 8$ Hz, 2H; C_6H_4); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 19.01$, 22.09, 23.32 (CH_3), 30.69 (CH(CH_3)$_2$), 48.44, 53.73, 61.49 (CH_2), 80.38, 80.72, 81.03, 81.42 (CH, cymene), 96.77, 99.09 (C, cymene), 114.86–143.86 (PC_6H_5, C_6H_4–CH=CH_2); elemental analysis calcd (%) for $C_{41}H_{45}N_2O_4PRuS$ (793.92): C 62.03, H 5.71, N 3.53; found C 62.36, H 6.00, N 3.37.

X-ray structure analysis of 5: Crystals of **5** were obtained by slow diffusion of hexane into a solution of **5** in dichloromethane. Enraf-Nonius diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.53 \times 0.47 \times 0.17$ mm, $T = 22(2)$ °C, orange crystal, monoclinic, space group $P2_1/c$, $a = 12.416(2)$, $b = 13.399(2)$, $c = 16.611(3)$ Å, $V = 2761.2(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.548$ Mg m^{-3}, $\mu = 1.054$ mm^{-1}. Data collection: ω from 2.45 to 23.97, $-14 \le h \le 14$, $-15 \le k \le 0$, $-18 \le l \le 0$, 4484 reflections collected, 4316 independent reflections ($R_{int} = 0.0143$), semiempirical absorption correction from psi-scans, max./min. transmission 0.9992/0.7506, $R_1 = 0.0598$, w$R_2 = 0.1592$ [$I >> 2\sigma(I)$], GOF(F^2) = 1.013, largest difference peak 0.651 e Å^{-3}, largest difference hole -1.125 e Å^{-3}. The structure was solved with direct methods (SHELXS-86). A riding model was employed for the hydrogen atoms. The vinyl groups as well as one methylene group are disordered and split positions with restraints were utilised. Restraints were also employed for the solvent molecule. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139602. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation of the polymers: A freshly prepared mixture of V-70 (15 mg) and EGDMA (934 μL, 4.95 mmol) was added to a solution of **4** (25 mg, 50 μmol) in $CHCl_3$ (400 μL) in a 4 mL screw-cap vial. After sonication (1 min) and degassing with dinitrogen (2 min), the vial was closed and tempered for 20 h at 35 °C, and then heated for 4 h at 65 °C. The resulting polymer was ground, wet-sieved (particle size: 25–100 μm), treated with a solution of [$BnNEt_3$]Cl in MeOH (40 mL, 0.1 M, 30 min), washed with MeOH (4×40 mL) and dried in vacuo. Polymers containing complex **6**, **7** or **8** were prepared in an analogous fashion.

Characterisation of the polymers: To determine the content of ruthenium and phosphorous in the polymers, the polymers (10–40 mg) were dissolved in a mixture of HNO_3 (conc., 0.5 mL) and HCl (conc., 0.5 mL) by heating to 120 °C for 4 h. After dilution with H_2O/HNO_3 (4 %), the amounts of ruthenium (±0.01 %) and phosphorous (±0.01 %) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a VARIAN Vista ICP-AES. The C/H analysis (±0.30 %) was carried out with a ELEMENTAR Vario EL. N_2 adsorption isotherms were measured on a Sorptomatic 1800 (Carlo Erba), which was controlled by the Milestone 200 program. For the polymers, a BET (BET = Brunauer–Emmet–Teller) inner surface area of 89 m^{2}g^{-1} was calculated from the experimental data in the range of relative pressures of $0.05 \le p/p_0 \le 0.35$ ($p_0 = N_2$ saturation pressure at liquid N_2 temperature). Prior to the measurements, samples were evacuated at 80 °C for 4 h. The apparent dry density of the polymers was determined to be 0.74 g mL^{-1}. The swelling, given as the volume of swollen polymer per volume of dry polymer, was determined to be 1.64 in acetonitrile.

Transfer hydrogenation of benzophenone

Method A: A suspension of the polymer (20.2 mg, 1 μmol Ru) in a mixture of azeotropic HCO_2H/NEt_3 (500 μL) and CH_3CN (400 μL) was stirred for 30 min at 70 °C (to calculate the amount of catalyst, a quantitative incorporation of the complexes into the polymer was assumed). The reaction was started by addition of benzophenone in CH_3CN (100 μL, 1 M). A sample (100 μL) was removed every five minutes from the reaction vessel, quenched with CH_3CN/CH_3CO_2H (3:1, 400 μL), filtered and analysed by capillary GC. Reactions with the imprinted polymer **P7** (**P8**) and the control polymer **P4** (**P6**) were performed simultaneously.

Method B: A suspension of the polymer (20.2 mg, 1 μmol Ru) in a solution of KOH (1.2 μmol) in 2-propanol (950 μL) was stirred for 15 min at 70 °C under an atmosphere of dinitrogen. The reaction was started by addition of benzophenone in 2-propanol (50 μL, 2 M) and analysed as described above.

Transfer hydrogenation of ketones S1–S7: A suspension of the polymer (20.2 mg, 1 μmol Ru) in a mixture of azeotropic HCO_2H/NEt_3 (500 μL) and CH_3CN (400 μL) was stirred for 30 min at 70 °C. The reaction was started by addition of **S1–S7** in CH_3CN (100 μL, 0.2 M each). After 20 min, a sample (200 μL) was removed from the reaction vessel, quenched with CH_3CN/CH_3CO_2H (2:1, 300 μL), filtered and analysed by capillary GC.

Transfer hydrogenation of 4-acetylbenzophenone: A suspension of the polymer (20.2 mg, 1 μmol Ru) in a mixture of azeotropic HCO_2H/NEt_3 (500 μL) and CH_3CN (500 μL) was stirred for 30 min at 70 °C. The reaction was started by addition of 4-acetylbenzophenone in CH_3CN (100 μL, 1 M). After 1 h, the suspension was diluted with dichloromethane (10 mL) and filtered immediately, and the solvent removed in vacuo. The residue was dissolved in $CDCl_3$ and analysed by ^{1}H NMR. The product distribution was determined by integration of the signals for the methyl groups.

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