Biomimetic Catalysis with an Immobilised Chiral Rhodium(III) Complex

Kurt Polborn[a] and Kay Severin*[a]

Keywords: Heterogeneous catalysis / Molecular imprinting / Hydrogenations / Transition states / Rhodium

An organometallic transition state analogue for the asymmetric reduction of acetophenone with a Cp*Rh complex has been synthesised and structurally characterised (**3**). This complex has a chiral *N*,*N*′-chelate ligand with a styrene side chain to allow its incorporation into organic polymers. The remaining coordination site is occupied by a methylphenylphosphinato ligand. This ligand acts as a pseudosubstrate which mimics acetophenone. The conformation and configuration of **3** in the crystal are in excellent agreement with the postulated transition structure. Following the protocol of molecular imprinting, complex **3** was co-polymerised with ethylene glycol dimethacrylate in the presence of a porogen. The resulting polymer **P3** was ground and sieved and the phosphinato ligand was substituted with a chloro ligand to generate a shape-selective cavity in proximity to the catalytically active metal centre. When tested for its ability to catalyse the reduction of acetophenone and related substrates the imprinted polymer **P3** showed a significantly higher activity than a control polymer **P2** without a cavity. Excellent enantioselectivities (up to 95% *ee*) were obtained, with the catalyst **P3** being more selective than the respective control catalyst **P2** (Δee = 2–9%). Competition experiments with acetophenone and a second co-substrate have revealed that the cavity generated with the phosphinato ligand is specific for acetophenone.

Introduction

Modern organometallic catalysts display high activities, some of which can rival those of metalloenzymes.[1] Nevertheless there is a fundamental difference in how the selectivity and activity is controlled in these systems. For (homogeneous) organometallic catalysts these parameters are mainly determined by the nature of the metal ion and the first coordination sphere.[2] For metalloenzymes, on the other hand, ligands of the second coordination sphere, that is, functional groups in the vicinity of the catalytically active centre, are crucial for chemical transformations. A well-defined microenvironment allows for the molecular recognition between enzyme and substrate and/or transition state and is thus the basis for high selectivity.

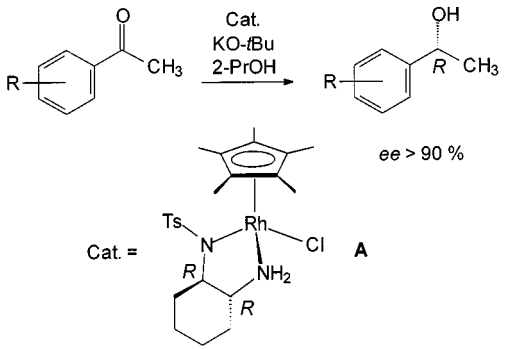
In recent years several approaches for manipulating the microenvironment of synthetic organometallic catalysts in a controlled fashion have been described. For example, catalytically active metal complexes have been covalently attached to organic host molecules (e.g. cyclodextrins)[3] or embedded into porous inorganic materials (e.g. zeolites).[4] However, most of these strategies either require substantial synthetic efforts or the obtained catalysts are rather unspecific. Recently, we have reported an alternative approach which combines the technology of molecular imprinting[5] with organometallic chemistry: a transition metal catalyst, having a polymerisable side chain, is co-polymerised with an organic crosslinking monomer. During the polymerisation a pseudosubstrate is coordinated to the catalytically active centre. Selective removal of the pseudosubstrate generates a complementary, shape selective cavity. The realisation of this concept was demonstrated for the Ru^{II}-catalysed transfer hydrogenation of benzophenone.[6] Here we describe the synthesis of a highly active and selective *chiral* Rh^{III} catalyst for the asymmetric reduction of acetophenone, obtained by molecular imprinting with a defined transition-state analogue (TSA).[7,8]

[a] Institut für Anorganische Chemie der
Ludwig-Maximilians-Universität,
Butenandtstraße 5–13, D-81377 München, Germany
E-mail: kse@cup.uni-muenchen.de

Results and Discussion

The asymmetric transfer hydrogenation of ketones and imines, catalysed by chiral complexes of the late transition metals has received considerable attention in recent years.[9] In particular, chiral (arene)Ru^{II} catalysts have been shown to be highly selective. Excellent results have also been obtained with the Cp*Rh complex **A** (Scheme 1): for the reduction of acetophenone and derivatives with 2-propanol in the presence of base an enantiomeric excess of more than 90% *ee* was observed.[10]

All experimental data for this reaction point to a cyclic transition state with a hydrogen bond from the carbonyl O-



Scheme 1. Asymmetric transfer hydrogenation of aromatic ketones with a chiral rhodium(III) catalyst[10a]

  1434–1948/00/0808–1687 $ 17.50+.50/0

atom to the adjacent amine group. Theoretical investigations on related Ru-catalysed reactions have provided additional evidence for such a geometry (Figure 1).[11] We propose a phosphinato complex as a TSA for the asymmetric reduction of acetophenone.

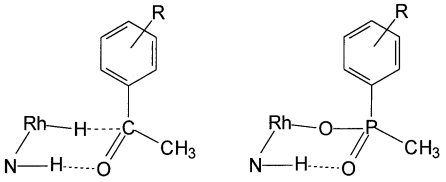
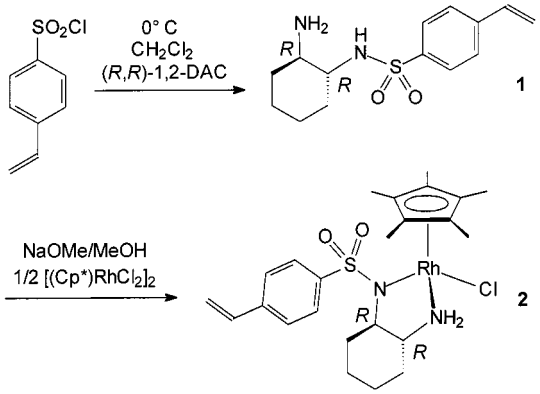


Figure 1. Postulated transition structure for the Rh^{III}-catalysed transfer hydrogenation of aromatic ketones (left); transition-state analogue with a phosphinato ligand (right)

Here we describe the synthesis and the structure of a polymerisable $CpRh^{III}$ catalysts with a methylphenylposphinato ligand. To allow catalysts of this kind to be incorporated into organic polymers we have synthesised a ligand with a styrene instead of a tolyl side chain. This was accomplished by condensation of (1*R*,2*R*)-1,2-diaminocyclohexane with *p*-styrylsulfonyl chloride (**1**). The rhodium complex **2** was obtained in good yields by reaction of **1** with $[Cp^*RhCl_2]_2$ in the presence of NaOMe (Scheme 2). The ^1H NMR spectrum of **2** shows only one set of signals ($CDCl_3$). This indicates that the synthesis is completely diastereoselective.

The structure of the racemic[12] complex **2** in the crystal is depicted in Figure 2. The coordination around the rhodium



Scheme 2. Synthesis of complex **2**

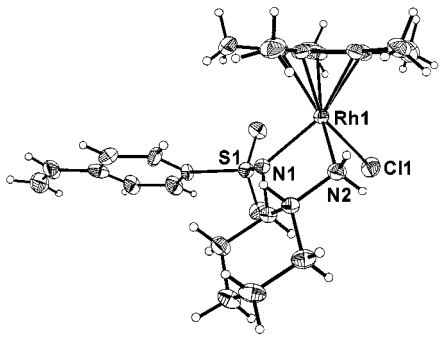
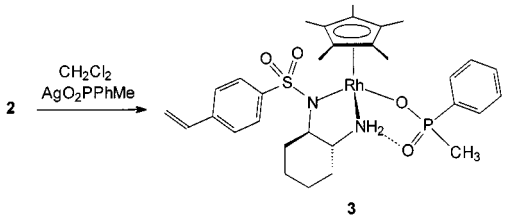


Figure 2. Structure of one enantiomer[12] of **2** in the crystal; selected bond length [Å] and angles [°]: Rh(1)−Cl(1) 2.416(2), Rh(1)−N(1) 2.152(4), Rh(1)−N(2) 2.120(4); N(2)−Rh(1)−N(1) 79.0(2), N(2)−Rh(1)−Cl(1) 82.23(13), N(1)−Rh(1)−Cl(1) 89.65(12)

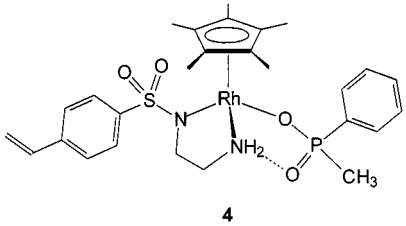
atom can be described as distorted octahedral with a bidentate, monoanionic amine ligand. The structure is similar to that found for the Cp*Rh complex **A**.[10a] Importantly, they have the same relative configuration of the rhodium atom with respect to the chiral ligand. The same relative configuration is also observed for structurally related (arene)Ru^{II} complexes.[13]

Substitution of the chloro ligand with the pseudosubstrate − the phosphinato ligand − is achieved by reaction of **2** with silver methylphenylphosphinate (Scheme 3). The resulting complex **3** has four stereogenic centres: the two carbon atoms of the amine ligand, the rhodium atom and the phosphorous atom. Four stereoisomers, which should be distinguishable by NMR spectroscopy, are thus expected. Again, however, the NMR spectra show only one set of signals ($CDCl_3$). This points to the fact that the configuration of the metal atom, as well as that of the phosphorous atom is controlled by the ligand, meaning that the chiral information is transferred with high efficiency from the ligand to the metal atom and the pseudosubstrate.



Scheme 3. Synthesis of complex **3**

It is important to note that the free phosphinato ligand is optically inactive. To determine the configurational stability of the phosphinato ligand coordinated to the rhodium atom we have synthesised complex **4** which bears an achiral chelate ligand. NMR experiments with this complex have shown that the configurational stability of the phosphinato ligand in **4** is very low. Most likely, the same is true for complex **3**.



The result of a single crystal analysis of racemic[12] **3** is shown in Figure 3. As is the case for compound **2**, the metal atom in **3** has the opposite configuration to that of the ligand. The coordination of the phosphinato ligand corresponds exactly to the postulated transition state: a monodentate coordination to the rhodium atom and a hydrogen bond to the adjacent amine group is observed. Based on quantum chemical calculations about the transition state of related (arene)Ru(aminoalcoholate) complexes Andersson et al. have predicted a strong preference for an almost planar H−Ru−N−H unit, with an energetic minimum obtained for H−Ru−N−H = 10°.[11a] Remarkably, this is exactly the value found for the corresponding angle in com-

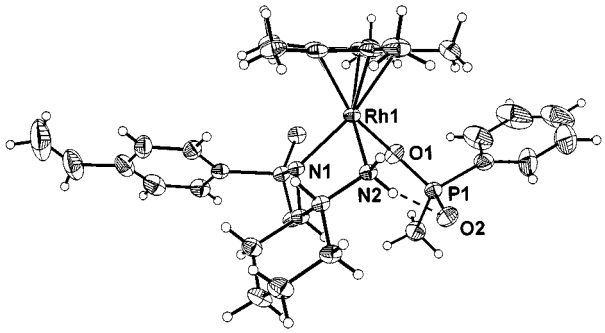
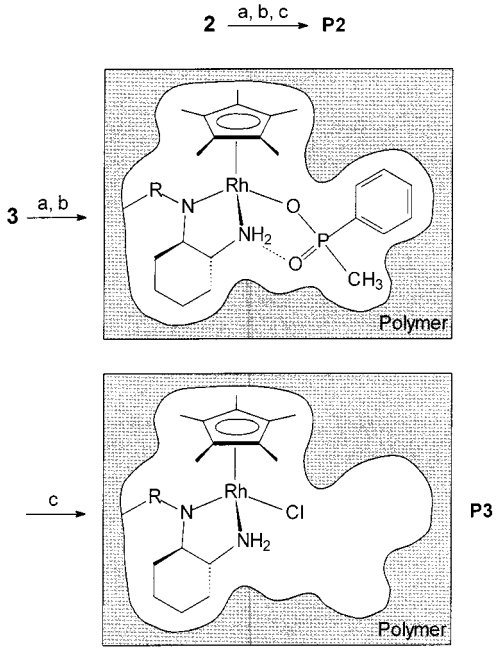


Figure 3. Structure of one enantiomer[12] of **3** in the crystal; selected bond length [Å] and angles [°]: Rh(1)−O(1) 2.131(2), Rh(1)−N(1) 2.142(4), Rh(1)−N(2) 2.120(4), P(1)−O(2) 1.489(3), P(1)−O(1) 1.504(3); N(2)−Rh(1)−N(1) 78.52(12), N(2)−Rh(1)−O(1) 88.59(12), N(1)−Rh(1)−O(1) 86.83(12)

plex **3** in the crystal (O1−Rh1−N2−H = 9.9°). From experiments with the homogeneous catalyst **A** it was observed that the reduction of acetophenone gives *R*-1-phenylethanol with high selectivity.[10a] For the transition structure a *syn*-configuration of the aryl group of the phosphinato ligand and the Cp* ring is therefore predicted. And indeed, this is the geometry which is observed for **3**. These results confirm that **3** is an excellent analogue for the transition state of the asymmetric reduction of acetophenone.

Immobilisation of the catalyst precursors **2** and **3** was achieved by co-polymerisation with ethylene glycol dimethacrylate (EGDMA) in the presence of a porogen ($CHCl_3$/MeOH, 4:1). The combination of EGDMA and $CHCl_3$ has previously been shown to be well suited for imprinting studies.[6,14] 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) was employed as the thermal initiator. The polymers **P2** and **P3** were ground and sieved to obtain a uniform particle size (25−100 μm). The orange powders were subsequently stirred in a solution of benzyltriethylammonium chloride in methanol (0.1 M), a procedure which selectively cleaves off the phosphinato ligand.[15] Therefore, both polymers have an almost identical chemical composition. Contrary to polymer **P2**, the molecularly imprinted polymer (MIP) **P3** has shape-selective cavities in proximity to the catalytically active centre of the rhodium complexes (Scheme 4).

To test the activity and enantioselectivity of the polymeric catalysts **P2** and **P3** we investigated the reduction of acetophenone with 2-propanol in the presence of KOH. For reactions with 1 mol-% **P2** after 6 h (*R*)-1-phenylethanol was obtained with 93% *ee* in 41% yield (Table 1). In the presence of the imprinted polymer **P3** the yield was increased to 81% with an optical purity of 95% *ee*. A similar increase in activity (the initial turnover frequencies differ by more than a factor of two) and selectivity (Δee = 2−8%) was observed for sterically related monohalogenated substrates. A significant difference in the enantioselectivity (Δee = 9%) was also detected in reactions with the more bulky substrate 1-acetonaphthone. These results show that the cavity generated by molecular imprinting has a pronounced effect on the activity of the immobilised catalyst. Furthermore, the expected decrease in selectivity of the heterogeneous catalyst **P2** as compared to the homogeneous version **A** is nearly abolished with the MIP catalyst **P3**. The increased enantioselectivity of **P3** (Δee = 2−9%) is most likely the result of additional space around the catalytically active rhodium complexes. The contribution of chiral cavities is less probable due to the low configurational stability of the pseudosubstrate. Overall, the imprinted catalyst **P3** displays an activity and selectivity which can compete with the homogeneous catalyst **A**[10] and which is higher than the values obtained with other homogeneous Cp*Rh catalysts.[10b,16] Compared to supported catalysts for the transfer hydrogenation of acetophenone, **P3** occupies a top position.[8a,17,18]



Scheme 4. Synthesis of the control polymer **P2** and the imprinted polymer **P3**: a) EGDMA, $CHCl_3$/CH_3OH, V-70, 24 h, 35 °C; b) 4 h, 65 °C; c) $[NEt_4]Cl$, CH_3OH

Table 1. Transfer hydrogenation of aromatic ketones in the presence of the imprinted catalyst **P3** and the control catalyst **P2**

Catalyst	Ketone	Time [h]	Yield [%]	*ee* [%][a]
P3 (**P2**)	Acetophenone	6	81 (41)	95 (93)
P3 (**P2**)	*p*-Fluoroacetophenone	6	71 (36)	93 (90)
P3 (**P2**)	*o*-Fluoroacetophenone	6	85 (52)	84 (76)
P3 (**P2**)	*m*-Fluoroacetophenone	3	98 (75)	94 (92)
P3 (**P2**)	*m*-Chloroacetophenone	3	98 (69)	94 (92)
P3 (**P2**)	1-Acetonaphthone	6	52 (24)	83 (74)

[a] In all cases the main isomer has the configuration *R*.

The substrate specificity was determined in competition experiments. The kinetics of the reduction of a mixture of acetophenone and a second substrate in the presence of **P2** or **P3** was investigated (ketone1/ketone2/catalyst = 50:50:1). Aliphatic and aromatic ketones, which differ in size and reactivity, were chosen as co-substrates. A comparison of the initial reaction rates revealed that in *all* cases the imprinted polymer **P3** displays a higher selectivity for

Table 2. Substrate selectivity of the polymeric catalysts **P2** and **P3**

Co-substrate	Selectivity[a] P3	Selectivity[a] P2
Cyclohexanone	$3.8\ 10^{-1}$	$3.1\ 10^{-1}$
2-Adamantanone	1.4	1.1
Benzophenone	$1.4\ 10^{1}$	8.9
α-Tetralone	4.2	3.7
2-Acetylnaphthalene	$8.9\ 10^{-1}$	$7.7\ 10^{-1}$

[a] The selectivity is calculated by dividing the initial rate of 1-phenylethanol formation by the initial rate of product formation for the reduction of the co-substrate.

acetophenone than the control polymer **P2** (Table 2), although the substrate selectivity is lower than that found for the immobilised ruthenium complexes previously described.[6] In accordance with the molecular structure determined for **3**, these kinetic studies prove that the methylphenylphosphinato ligand represents an excellent pseudosubstrate for acetophenone and leaves a *specific* and *shape-selective* imprint in the polymeric matrix.

Conclusions

We have shown that heterogeneous catalysts for the asymmetric transfer hydrogenation of aromatic ketones are available by immobilisation of the chiral rhodium complexes **2** and **3**, both of which were structurally characterised. The microenvironment of the polymeric catalyst **P3** was modified in a controlled fashion by molecular imprinting with the organometallic TSA **3**. As a result an enhanced activity combined with an excellent enantioselectivity was observed for the reduction of acetophenone and related substrates. Kinetic experiments have revealed that the cavity generated by imprinting is specific for acetophenone.

The concept presented in this paper for the construction of shape selective cavities in proximity to the catalytically active centre of organometallic catalysts is very simple and flexible. The results prove that this method is suitable for generating heterogeneous catalysts with a superior performance in asymmetric reactions even when optically inactive pseudosubstrates are employed. It appears likely that this methodology is applicable to other catalysts and reactions. Research along these lines may ultimately lead to tailor-made organometallic catalysts with enzyme-like characteristics.

Experimental Section

General: The synthesis of all complexes as well as the transfer hydrogenation was performed under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and stored under nitrogen prior to usage. EGDMA was washed with NaOH (1 M) 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 obtained from Wako Chemicals. AgO_2PPhMe was obtained as a white precipitate by reaction of KO_2PPhMe with $AgNO_3$. The synthesis of $[Cp^*Rh(NH_2CH_2CH_2NSO_2C_8H_7)Cl]$ was carried out analogously to that of **2** using the achiral ligand $NH_2CH_2CH_2NHSO_2C_8H_7$.[6b] 4-Vinyl-benzenesulfonyl chloride[18] and $[Cp^*RhCl_2]_2$[19] 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 with the solvent as the internal standard. All spectra were recorded at room temperature; exceptions are indicated. The GC analysis was performed with a Varian 3800 spectrometer using a CP-Cyclodextrin-B-2,3,6-M-19 column (50 m).

Synthesis of Ligand 1: A solution of *p*-styrylsulfonyl chloride (816 μL) in CH_2Cl_2 (30 mL) was added slowly (1 h) to a solution of (*R*,*R*)-1,2-diaminocyclohexane (1.84 g, 16.1 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was warmed to room temperature, filtered and the solvent was removed under reduced pressure. The product was purified by flash chromatography with EtOAc/MeOH (3:2) and crystallised from CH_2Cl_2/hexane. Yield: 730 mg (16%, referred to the amine), m.p. 105−107 °C. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.04−1.26 (m, 4 H, CH_2), 1.57−1.95 (m, 4 H, CH_2), 2.37−2.46 (m, 1 H, CHN), 2.63−2.72 (m, 1 H, CHN), 3.04 (s, br, 3 H, NH_2, NH), 5.41 (d, ^3J = 11 Hz, 1 H, CH=CH_2), 5.87 (d, ^3J = 18 Hz, 1 H, CH=CH_2), 6.73 (dd, ^3J = 11 Hz, ^3J = 18 Hz, 1 H, CH=CH_2), 7.51 (d, ^3J = 8 Hz, 1 H, C_6H_4), 7.85 (d, ^3J = 8 Hz, 1 H, C_6H_4). − ^{13}C NMR (68 MHz, $CDCl_3$):δ = 24.8, 25.0, 32.7, 35.5 (CH_2), 54.8, 60.3 (NCH), 117.3, 126.8, 127.5, 135.5, 139.9, 141.7 (C_6H_4−CH=CH_2). − $C_{14}H_{20}N_2O_2S\cdot 1/3H_2O$ (286.39): calcd. C 58.72, H 7.27, N 9.78; found C 58.91, H 7.67, N 9.70.

Synthesis of Complex 2: A solution of (1*R*,2*R*)-*N*-(*p*-styrylsulfonyl)-1,2-diaminocyclohexane (280 mg, 1.0 mmol) and NaOMe (1.0 mmol, 2.37 M in MeOH) in CH_2Cl_2/MeOH (20 mL, 1:1) was added slowly to a solution of $[Cp^*RhCl_2]_2$ (309 mg, 0.5 mmol) in CH_2Cl_2 (20 mL). After stirring for 2 h the solvent was removed under reduced pressure and the product was extracted with CH_2Cl_2 (30 mL). After addition of hexane (20 mL) the solvent was removed under reduced pressure to give a yellow powder which was dried in vacuo. Yield: 451 mg (79%), m.p. 225−227 °C (dec.). − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.81−1.98 (m, 7 H, CH_2), 1.74 (s, 15 H, Cp*), 2.23−2.30 (m, 3 H, NCH, CH_2), 2.99−3.02 (m, 1 H, NH), 3.38−3.42 (m, 1 H, NH), 5.27 (d, ^3J = 11 Hz, 1 H, CH=CH_2), 5.77 (d, ^3J = 18 Hz, 1 H, CH=CH_2), 6.70 (dd, ^3J = 11 Hz, ^3J = 18 Hz, 1 H, CH=CH_2), 7.39 (d, ^3J = 8 Hz, 2 H, C_6H_4), 8.02 (d, ^3J = 8 Hz, 2 H, C_6H_4). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.7 (CH_3, Cp*), 24.6, 24.9, 34.6, 36.3 (CH_2), 63.5, 64.4 (NCH), 94.0 (d, $^1J_{RhC}$ = 8 Hz, C, Cp*) 115.1, 125.9, 128.3, 136.4, 139.0, 145.4 (C_6H_4−CH=CH_2). − $C_{24}H_{34}ClN_2O_2RhS\cdot H_2O$ (570.97): calcd. C 50.49, H 6.36, N 4.91; found C 50.77, H 6.09, N 4.82.

Synthesis of Complex 3: A suspension of **2** (111 mg, 0.20 mmol) and AgO_2PPhMe (58 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was stirred for 96 h at room temperature. The solid products were removed by filtration and the solvent was reduced to a volume of 2 mL. After addition of hexane the solvent was removed in vacuo to give an orange powder which was dried in vacuo. Yield: 119 mg (86%), m.p. 148−150 °C (dec.). − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.61−1.57 (m, 6 H, CH_2), 1.33 (d, $^2J_{PH}$ = 14 Hz, 3 H, PCH_3), 1.48 (s, 15 H, Cp*), 1.84−2.07 (m, 3 H, NCH, CH_2), 2.29−2.37 (m, 1 H, NCH), 5.20 (d, ^3J = 11 Hz, 1 H, CH=CH_2), 5.68 (d, ^3J = 17 Hz, 1 H, CH=CH_2), 6.60 (dd, ^3J = 11 Hz, ^3J = 17 Hz, 1 H, CH=CH_2), 7.26−7.30 (m, 5 H, PPh, C_6H_4), 7.66−7.77 (m, 4 H, PPh, C_6H_4). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.5 (CH_3, Cp*), 18.8 (d, $^1J_{PC}$ = 99 Hz, PCH_3), 24.4, 24.6, 33.9, 35.0 (CH_2), 63.3, 63.8 (NCH), 93.7 (d, $^1J_{RhC}$ = 9 Hz, C, Cp*) 115.5, 125.9,

Table 3. Crystallographic data of **2** and **3**

	2	**3**
Empirical formula	$C_{24}H_{34}ClN_2O_2RhS$	$C_{31}H_{42}N_2O_4PRhS{\cdot}0.5{\cdot}CH_2Cl_2$
Molecular weight [g mol^{-1}]	552.95	715.07
Crystal size	0.10 × 0.20 × 0.30	0.20 × 0.33 × 0.53
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.500(1)	9.1575(1)
b [Å]	12.525(3)	14.569(4)
c [Å]	21.364(5)	26.831(5)
β [°]	94.52(2)	93.578(13)
Volume [Å^3]	2534(1)	3572(1)
Z	4	4
Density [g cm^{-3}]	1.449	1.329
Absorption coefficient [mm^{-1}]	0.884	0.691
Θ range [°]	2.15 to 23.99	2.62 to 23.98
Index ranges	−7 → 10, −0 → 14, −24 → 24	−10 → 0, −16 → 0, −30 → 30
Reflections collected	4240	5976
Independent reflections	3965 (R_{int} = 0.0390)	5586 (R_{int} = 0.0314)
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.9990 and 0.8758	0.9999 and 0.9333
Weights	$w = 1/(\sigma^2(F_0^2) + (0.0332P)^2 + 4.3928P]$; $P = (F_0^2 + 2F_c^2)/3$	$w = 1/(\sigma^2(F_0^2) + (0.0598P)^2 + 2.6744P]$; $P = (F_0^2 + 2F_c^2)/3$
Data/restraints/parameters	3122/8/323	4680/21/394
Goodness-of-fit on F^2	1.201	1.159
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0407, $wR2$ = 0.0866	$R1$ = 0.0391, $wR2$ = 0.1043
R indices (all data)	$R1$ = 0.0602, $wR2$ = 0.1020	$R1$ = 0.0500, $wR2$ = 0.1125
Largest diff. peak/hole [eÅ^{-3}]	0.487/−0.390	0.848/−0.457

126.9 (C_6H_4−CH=CH_2), 127.8−130.5 (m, PPh), 135.8, 139.6, 146.9 (C_6H_4−CH=CH_2). − ^{31}P NMR (109 MHz, $CDCl_3$):δ = 40.0. − $C_{31}H_{42}N_2O_4PRhS{\cdot}H_2O$ (690.64): calcd. C 53.91, H 6.42, N 4.06; found C 54.04, H 6.75, N 3.93.

Synthesis of Complex 4: The synthesis of **4** was carried out analogously to that of **3** using [Cp*Rh($NH_2CH2CH2NSO_2C_8H_7$)Cl] (100 mg, 0.20 mmol) and AgO_2PPhMe (58 mg, 0.22 mmol). Yield: 109 mg (86%), m.p. 120−122 °C (dec.). − ^{1}H NMR (270 MHz, CD_3OD): δ = 1.34 (d, $^2J_{PH}$ = 14 Hz, 3 H, PCH_3), 1.66 (s, 15 H, Cp*), 2.46−2.50 (m, 2 H, CH_2), 2.62−2.66 (m, 1 H, CH_2), 5.34 (d, ^3J = 11 Hz, 1 H, CH=CH_2), 5.89 (d, ^3J = 18 Hz, 1 H, CH=CH_2), 6.77 (dd, ^3J = 11 Hz, ^3J = 18 Hz, 1 H, CH=CH_2), 7.39−7.82 (m, 9 H, PPh, C_6H_4). − ^{13}C NMR (68 MHz, CD_3OD): δ = 8.2 (CH_3, Cp*), 17.8 (d, $^1J_{PC}$ = 99 Hz, PCH_3), 45.7, 50.3 (CH_2), 94.5 (d, $^1J_{RhC}$ = 9 Hz, C, Cp*) 115.5−142.7 (m, C_6H_4−CH=CH_2, PPh). − ^{31}P NMR (109 MHz, CD_3OD):δ = 31.0. − $C_{27}H_{36}N_2O_4PRhS{\cdot}H_2O$ (636.54): calcd. C 50.95, H 6.02, N 4.40; found C 51.37, H 6.07, N 4.10.

Synthesis of Polymer P2: A freshly prepared mixture of V-70 (15 mg) and EGDMA (4.95 mmol) was added to a solution of **2** (50 μmol) in $CHCl_3$/MeOH (467 μL, 4:1) in a 4 mL screw-cap vial. The orange solution was sonicated (1 min) and degassed with nitrogen (2 min). The vial was closed and tempered at 35 °C (24 h) and then at 65 °C (3 h). The obtained polymer was ground, sieved (particle size: 25−100 μm) and stirred in a solution of benzyltriethylammonium chloride in MeOH (0.1 M). The polymer was isolated, washed with MeOH (4 × 40 mL) and dried in vacuo. The synthesis of the polymer **P3** was performed analogously to that of **P2** using complex **3** (50 μmol).

X-ray Crystallographic Investigations: An Enraf Nonius CAD 4 diffractometer was employed for data collection using Mo-K_α radiation (T = 295 K). The structures were solved by direct methods (SHELXS86) and were refined by means of the full-matrix least-squares procedures using SHELXL93 (Table 3). All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. The styryl groups of **2** is disordered. Restraints were used for parts of the aromatic ring. Compound **3** crystallizes together with 0.5 molecules of dichloromethane. The solvent molecules are disordered and restraints were used for the refinement.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136894 (**2**) and CCDC-136895 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Transfer Hydrogenations: A suspension of **P2** (20.2 mg, this corresponds to 1.0 μmol Rh if a quantitative incorporation is assumed) in 2-propanol containing 1.2 μmol KOH were stirred for 15 min at 33 °C. The reaction was started by addition of the substrate in 2-propanol. The initial concentration of the substrate was 0.1 M (0.5 M for competition experiments) with a total volume of 1 mL. Samples were removed at the times indicated, quenched with 2-propanol/EtOAc (3:1), filtered and analysed by capillary GC (CP-cyclodextrin-B-2,3,6-M-19 column by Chrompack, 50 m). For competition experiments the course of the reaction was analysed for the first 12 min. Reactions with the imprinted polymer **P3** were performed simultaneously and under identical conditions.

Acknowledgments

K. S. thanks Prof. Dr. W. Beck (LMU München) for his generous support and E. Karaghiosoff for technical assistance. Financial funding from the Bayerischer Habilitations-Förderpreis (K. S.) is gratefully acknowledged.

[1] A turnover frequency (TOF) of more than 10^5 h^{-1} was observed for ruthenium(II)-catalysed hydrogenations or for the alkene polymerisation with metallocene catalysts: [1a] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem.*

1998, *110*, 1792−1796; *Angew. Chem. Int. Ed.* **1998**, *37*, 1703−1707. − [1b] H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, *Angew. Chem*. **1995**, *107*, 1255−1283; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 1143.

[2] Exceptions are organometallic Lewis acids, the reactivity of which is often influenced by the second coordination sphere. For example see: E. P. Kündig, C. M. Saudan, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 1298−1301; *Angew. Chem. Int. Ed.* **1999**, *38*, 1220−1223.

[3] [3a] M. T. Reetz, S. R. Waldvogel, *Angew. Chem*. **1997**, *109*, 870−873; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 865−867. − [3b] M. T. Reetz, C. Frömbgen, *Synthesis* **1999**, *9*, 1555−1557. − [3c] R. Breslow, S. D. Dong, *Chem. Rev.* **1998**, *98*, 1997−2011.

[4] [4a] J. M. Thomas, *Angew. Chem*. **1999**, *111*, 3800−3843; *Angew. Chem. Int. Ed.* **1999**, *38*, 3588−3628. − [4b] E. J. Creyghton, R. S. Downing, *J. Mol. Cat. A* **1998**, *134*, 47−61.

[5] [5a] K. Haupt, K. Mosbach, *Trends Biotech.* **1998**, *16*, 468−475. − [5b] G. Wulff, *Angew. Chem*. **1995**, *107*, 1958−1979; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1812−1832. − [5c] *Molecular and Ionic Recognition with Imprinted Polymers* (Eds.: R. A. Bartsch, M. Maeda Oxford University Press, New York, **1998**.

[6] [6a] K. Polborn, K. Severin, *Chem. Commun.* **1999**, 2481−2482. − [6b] K. Polborn, K. Severin, *Chem. Eur. J.*, submitted for publication.

[7] Strategies to design catalysts with the help of TSAs have been summarised: [7a] P. A. Brady, J. K. M. Sanders, *Chem. Soc. Rev.* **1997**, *26*, 327−336. − [7b] J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 1378−1383. − [7c] M. E. Davies, A. Katz, W. R. Ahmad, *Chem. Mater.* **1996**, *8*, 1820−1839.

[8] Mosbach and Lemaire have utilised classical coordination compounds to obtain catalytically active polymers by molecular imprinting. The pseudosubstrate complexes were prepared in situ prior to polymerisation and were not further characterised: [8a] P. Gamez, B. Dunjic, C. Pinel, M. Lemaire, *Tetrahedron Lett*. **1995**, *36*, 8779−8782. − [8b] F. Locatelli, P. Gamez, M. Lemaire, *J. Mol. Catal. A* **1998**, *135*, 89−98. − [8c] J. Matsui, I. A. Nicholls, I. Karube, K. Mosbach, *J. Org. Chem.* **1996**, *61*, 5414−5417.

[9] [9a] M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045−2061. − [9b] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97−102.

[10] [10a] K. Murata, T. Ikariya, R. Noyori, *J. Org. Chem*. **1999**, *64*, 2186−2187; related Rh^{III}- and Ir^{III} catalysts with *N*-*p*-toluenesulfonyl-1,2-diphenylenediamine ligands have been described: [10b] K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1199−1200. − [10c] J. Mao, D. C. Baker, *Org. Lett.* **1999**, *1*, 841−843.

[11] [11a] D. A. Alonso, P. Brandt, S. J. M. Nordin, P. G. Andersson, *J. Am. Chem. Soc.* **1999**, *121*, 9580−9588. − [11b] M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466−1478.

[12] To obtain single crystals of **2** and **3** complexes with a racemic ligand (*R*,*R* and *S*,*S*) were employed.

[13] [13a] K.-J. Haak, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 297−300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285−288. − [13b] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562−7563.

[14]] [14a] J. Matsui, Y. Miyoshi, O. Doblhoff-Dier, T. Takeushi, *Anal. Chem.* **1995**, *67*, 4404−4408. − [14b] B. Sellergren, K. J. Shea, *J. Chromatogr.* **1993**, *635*, 31−49. − [14c] G. Vlatakis, L. I. Andersson, R. Müller, K. Mosbach, *Nature* **1993**, *361*, 645−647.

[15] Upon addition of benzyltriethylammonium chloride to a solution of **3** a quantitative exchange of the phosphinato is observed. This was shown by in situ NMR experiments (^{31}P, ^{1}H).

[16] D. Carmona, F. J. Lahoz, R. Atencio, L. A. Oro, M. P. Lamata, F. Viguri, E. San José, C. Vega, J. Reyes, F. Joó, A. Kathó, *Chem. Eur. J.* **1999**, 1544−1564.

[17] [17a] D. J. Bayston, C. B. Travers, M. E. C. Polywka, *Tetrahedron Asymmetry* **1998**, *9*, 2015−2018. − [17b] R. ter Halle, E. Schulz, M. Lamaire, *Synlett* **1997**, 1257−1258. − [17c] E. Breysse, C. Pinel, M. Lemaire, *Tetrahedron: Asymmetry* **1998**, *9*, 879−900.

[18] H. Kamogawa, A. Kanzawa, M. Kadoya, T. Naito, M. Nanasawa, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 762−765.

[19] C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228−230.

Received February 29, 2000
[I00077]