

Fluorinated Alcohols as Solvents for Enantioselective Hydrogenation with Chiral Self-Assembling Rhodium Catalysts

Natalia V. Dubrovina,^{a,*} Ivan A. Shuklov,^a Mandy-Nicole Birkholz,^a
Dirk Michalik,^a Rocco Paciello,^b and Armin Börner^{a,c,*}

^a Leibniz-Institut für Katalyse an der Universität Rostock e.V., A.-Einstein-Str. 29a, 18059 Rostock, Germany

Fax: (+49)-381-1281-51202; e-mail: armin.boerner@catalysis.de or natalia.dubrovina@catalysis.de

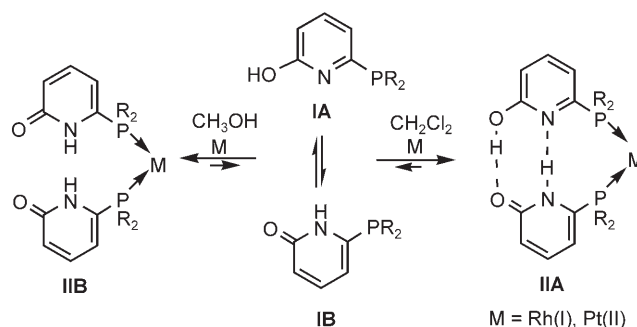
^b BASF AG, Basic Chemicals Research, GCB/O – M 313, 67056 Ludwigshafen, Germany

^c Institut für Chemie der Universität Rostock, A.-Einstein-Str. 3a, 18059 Rostock, Germany

Received: April 10, 2007; Published online: September 11, 2007

Abstract: We herein describe the beneficial effect of fluorinated alcohols on asymmetric hydrogenation using chiral self-assembling rhodium complexes. Previously, the application of these catalysts has been hampered by low reaction rates in non-polar solvents, which are essential for establishing the self-assembling architecture *via* hydrogen bonding. Excellent reaction rates are usually observed in alcohols as solvents, but the characteristic hydrogen bonds are cleaved in those media, resulting in poor *ee* values. We now show for the first time that the disadvantageous properties of both solvent classes on the catalytic reaction can be overcome by using fluorinated alcohols. Due to this key finding, homogeneous catalysis with self-assembling catalysts is much closer to practical application.

Keywords: asymmetric catalysis; hydrogenation; phosphane ligands; rhodium; self-assembly; solvent effects



Scheme 1. Self-assembly of 6-phosphanyl-2-pyridone in the presence of a transition metal salt in dependence on the solvent.

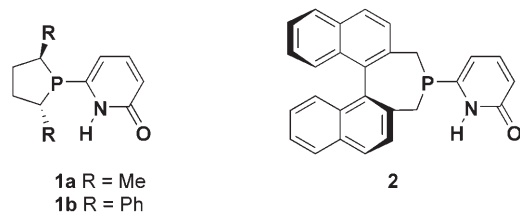
Rhodium(I) complexes of **IIA** derived from this system turned out to be highly efficient in the regioselective hydroformylation.^[4a-c] Moreover, P ligands equipped with complementary H-bonding motifs, on the basis of an A–T base pair analogy, have been prepared and advantageously employed in a combinatorial approach.^[5] The concept was extended to the Ru-catalyzed hydration of nitriles^[4d] and *anti*-Markovnikov hydration of terminal alkynes.^[4e] Furthermore, in an HTS approach, a library of self-assembling chiral phosphorus donor ligands has been studied in the course of Rh-catalyzed enantioselective hydrogenations.^[6] Hydrogen bonding has been also identified as a critical issue of chiral Rh catalysts bearing monodentate phosphoramidites by Ding and co-workers.^[7]

In a recent systematic study on the catalyzed enantioselective hydrogenation of dimethyl itaconate and methyl α -(*Z*)-*N*-acetamidocinnamate with cationic Rh complexes, we reported evidence that the efficiency of the reaction is strongly dependent on the bulk of the chiral phosphine moiety as well as on the solvent used.^[8] Superior enantioselectivities (99% *ee*) were observed with phosphine **2** as ligand in comparison to phospholanes **1a**, **b** in the non-polar solvent CH₂Cl₂. Unfortunately, slow conversion was noted in

The application of self-assembling catalysts has been established in recent years as a valued alternative to the employment of metal complexes based on conventional monodentate or bidentate ligands within the field of metal-catalyzed homogeneous catalysis.^[1,2] Amongst other aspects, such conformationally flexible chelates can better adapt to steric requirements of a substrate (“induced fit”).^[3] Additionally, a reduction in the synthetic work necessary to build libraries for screening is expected.

Impressive results have been documented by Breit et al. using the 6-phosphanyl-2-pyridone system **IB**, which self-assembles through hydrogen bonding with its tautomer **IA** in the presence of a late transition metal salt (Scheme 1).^[4]

most cases under these conditions. This was particularly pronounced for complexes bearing phospholane ligands **1a**, **b**. In contrast, in most cases enantioselective



tive hydrogenations proceeded faster in polar solvents like MeOH, but in this case low *ee* values in the range of 0 to 47% were observed. Detailed NMR spectroscopic investigation showed that self-assembly and therefore chelate formation only took place in non-polar solvents, whereas in CD₃OD the hydrogen bonds were broken and metal complexes bearing monodentate ligands formed (Scheme 1, **IIb**).

Obviously unique polar solvents are required which do not disturb the self-assembling architecture of the hydrogenation catalyst in order to maintain the beneficial effect of hydrogen bonding on the enantioselectivity. At the same time the low reaction rates must be overcome. As shown in Figure 1, fluorinated alcohols with low hydrogen bond acceptor properties

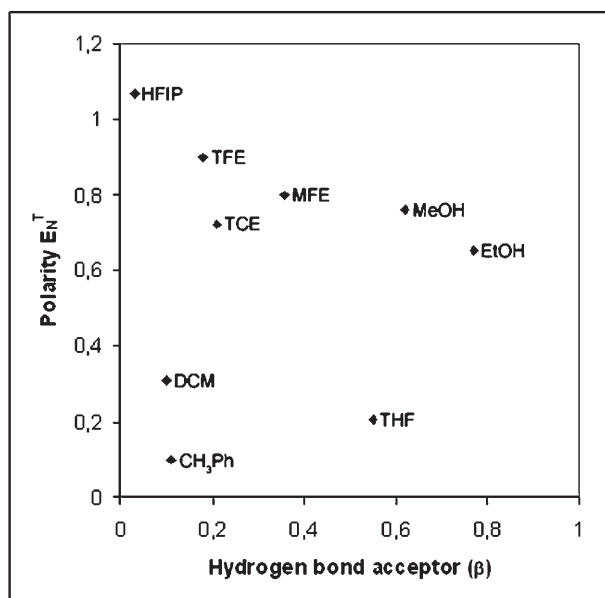


Figure 1. Correlation of the polarity (E_N^T) with hydrogen bond acceptor properties (β). HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol [CF₃CH(OH)CF₃], TFE = 2,2,2-trifluoroethanol [CF₃CH₂OH], MFE = 2-fluoroethanol [CH₂FCH₂OH], TCE = 2,2,2-trichloroethanol [CCl₃CH₂OH], DCM = dichloromethane [CH₂Cl₂], THF = tetrahydrofuran [C₄H₈O], MeOH = methanol [CH₃OH].^[9]

should be suitable solvents in terms of polarity and hydrogen bonding tolerance.

Indeed, NMR investigations of a cationic Rh-complex of **1a** in CF₃CD₂OD (Figure 2) showed a similar signal pattern as found in CDCl₃.^[8] Two doublets of doublets $\delta = 52.0$ [dd, $J(^{31}\text{P},^{103}\text{Rh}) = 147$ Hz, $J(^{31}\text{P},^{31}\text{P}) = 36$ Hz] and $\delta = 50.4$ [$J(^{31}\text{P},^{103}\text{Rh}) = 140$ Hz, $J(^{31}\text{P},^{31}\text{P}) = 36$ Hz] are characteristic.^[10] Due to the investigations and conclusions of the preceding paper these signals can be attributed to two different P groups: one attached to a pyridone and the other to a pyridinol scaffold. This is clear evidence that the self-assembly is completely maintained in the fluorinated alcohol. Moreover, signals at lower field usually observed in CDCl₃ and probably characterizing polymeric species^[11] or P,N complexes^[12] are not visible.

Results of the asymmetric hydrogenation of the benchmark substrates methyl *Z*- α -N-acetamidocinnamate and dimethyl itaconate are detailed in Table 1. For comparison, results measured in CH₂Cl₂ and MeOH are also listed.^[8]

Remarkably, the application of CF₃CH₂OH as solvent yielded similarly high *ee* values as those obtained in CH₂Cl₂.^[13] Moreover, with the exception of run 15, reactions proceeded much faster and the rates observed even exceed those achievable in the “favourite” solvent CH₃OH. Interestingly, other fluorinated solvents are also highly useful for this catalytic reaction. Thus, the use of CH₂FCH₂OH yielded similar superior results (runs 10 and 23). With CF₃CH(OH)CF₃, the reaction rate was lowered. However, in general, high enantioselectivities were obtained (runs 11 and 22). Remarkably, employment of CCl₃CH₂OH gave poor results (runs 12 and 24), which clearly shows the unique properties of the fluorinated alcohols.

In order to provide additional proof for the beneficial effect of self-assembling, the “ordinary” non-assembling monodentate ligands **3a**, **b** and **4** were tested

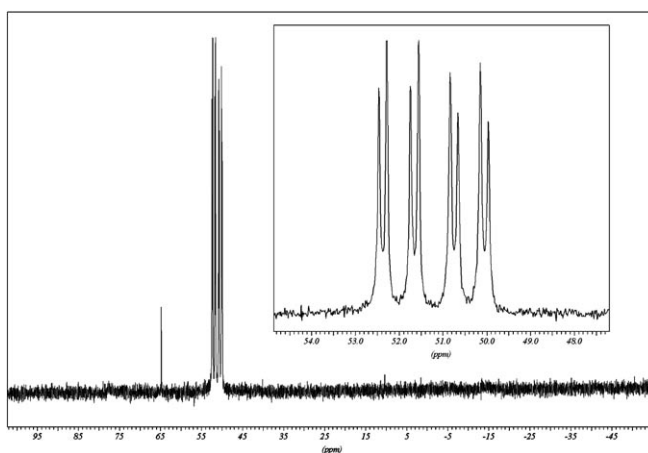


Figure 2. ³¹P NMR spectrum of [Rh(COD)(**1a**)₂]BF₄ in CF₃CD₂OD at 0 °C.

Table 1. Comparison of results of the enantioselective hydrogenation in different solvents.^[a]

Entry	Ligand	Substrate R ¹	R ²	Solvent	<i>t</i> [min]	Conversion [%]	<i>ee</i> [%]
1	1a ^[b]	NHAc	Ph	CH ₂ Cl ₂	1400	100	69 (<i>R</i>) ^[d,e]
2	1a ^[b]	NHAc	Ph	CH ₃ OH	1300	20	13 (<i>R</i>) ^[d,e]
3	1a ^[b]	NHAc	Ph	CF ₃ CH ₂ OH	1200	100	68 (<i>R</i>) ^[d]
4	1b ^[b]	NHAc	Ph	CH ₂ Cl ₂	3900	92	83 (<i>R</i>) ^[d,e]
5	1b ^[b]	NHAc	Ph	CH ₃ OH	2760	100	27 (<i>R</i>) ^[d,e]
6	1b ^[b]	NHAc	Ph	CF ₃ CH ₂ OH	1800	100	84 (<i>R</i>) ^[d]
7	2 ^[c]	NHAc	Ph	CH ₂ Cl ₂	10	100	94 (<i>R</i>) ^[d,e]
8	2 ^[c]	NHAc	Ph	CH ₃ OH	50	100	64 (<i>R</i>) ^[d,e]
9	2 ^[c]	NHAc	Ph	CF ₃ CH ₂ OH	10	100	95 (<i>R</i>) ^[d]
10	2 ^[b]	NHAc	Ph	CH ₂ FCH ₂ OH	6	100	96 (<i>R</i>) ^[d]
11	2 ^[b]	NHAc	Ph	CF ₃ CH(OH)CF ₃	800	100	94 (<i>R</i>) ^[d]
12	2 ^[b]	NHAc	Ph	CCl ₃ CH ₂ OH	1380	2	n.d.
13	1a ^[b]	CH ₂ COOMe	H	CH ₂ Cl ₂	1300	88	83 (<i>S</i>) ^[e,f]
14	1a ^[b]	CH ₂ COOMe	H	CH ₃ OH	400	100	rac ^[f]
15	1a ^[b]	CH ₂ COOMe	H	CF ₃ CH ₂ OH	1400	93	68 (<i>S</i>) ^e
16	1b ^[b]	CH ₂ COOMe	H	CH ₂ Cl ₂	2880	53	51 (<i>S</i>) ^[e,f]
17	1b ^[b]	CH ₂ COOMe	H	CH ₃ OH	2880	100	47 (<i>S</i>) ^[e,f]
18	1b ^[b]	CH ₂ COOMe	H	CF ₃ CH ₂ OH	300	100	40 (<i>S</i>) ^[f]
19	2 ^[c]	CH ₂ COOMe	H	CH ₂ Cl ₂	20	100	99 (<i>S</i>) ^[e,f]
20	2 ^[c]	CH ₂ COOMe	H	CH ₃ OH	60	100	64 (<i>S</i>) ^[e,f]
21	2 ^[c]	CH ₂ COOMe	H	CF ₃ CH ₂ OH	10	100	97 (<i>S</i>) ^[f]
22	2 ^[b]	CH ₂ COOMe	H	CF ₃ CH(OH)CF ₃	30	100	96 (<i>S</i>) ^[f]
23	2 ^[b]	CH ₂ COOMe	H	CH ₂ FCH ₂ OH	25	100	89 (<i>S</i>) ^[f]
24	2 ^[b]	CH ₂ COOMe	H	CCl ₃ CH ₂ OH	1050	1	n.d.

^[a] Conditions: Precatalyst generated *in situ* by reaction of [Rh(COD)₂]BF₄ with two equivs. of ligand.

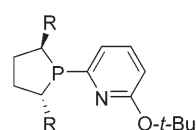
^[b] Substrate:catalyst = 50:1, 7.5 mL solvent.

^[c] Substrate:catalyst 100:1, 7.5 mL solvent.

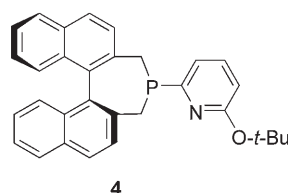
^[d] Determined by GC, 25 m γ -cyclodextrin, Lipodex E (Machery and Nagel), fused silica, 130 °C.

^[e] See Ref.^[8]

^[f] Determined by GC, 25 m γ -cyclodextrin, Lipodex E (Machery and Nagel), fused silica; 70 °C.



3a R = Me
3b R = Ph



4

in the enantioselective hydrogenation in CF₃CH₂OH as a solvent.

As it can be seen in Table 2 catalysts with non-assembling ligands induce much lower enantioselectivity. In accordance to results of the reaction in polar (CH₃OH) or non-polar solvents (CH₂Cl₂), where only small differences in *ee* values were noted,^[8] also only small deviations in CF₃CH₂OH are visible. These results give evidence that these catalysts work rather independent of the solvent used. In contrast, the cata-

lytic effect of complexes with self-assembling properties is strongly dependent on the solvent used.

In conclusion, the beneficial effect of fluorinated alcohols on the asymmetric hydrogenation with self-assembling catalyst has been documented for the first time. Due the broad availability of fluorinated solvents our findings are also of great practical importance.^[13] Moreover, our observation should also be of great importance for other catalysts bearing two monodentate ligands where intramolecular interactions *via* hydrogen bondings have been assumed.^[7,13g]

Experimental Section

General Remarks

All reactions involving phosphanes were performed under an inert atmosphere of argon by using standard Schlenk

Table 2. Comparison of results of the enantioselective hydrogenation with monodentate ligands **3a**, **b** and **4**.^[a]

$$\begin{array}{c}
 \text{H} \quad \text{COOMe} \\
 \diagdown \quad / \\
 \text{C} = \text{C} \\
 / \quad \diagdown \\
 \text{R}^2 \quad \text{R}^1
 \end{array}
 \xrightarrow[\text{H}_2 \text{ (1 bar), r.t.}]{[\text{Rh}(\text{COD})_2]\text{BF}_4 + 2 \text{ equivs. ligand,}}
 \begin{array}{c}
 \text{H} \quad \text{COOMe} \\
 | \quad / \\
 \text{C} - \text{C} \\
 / \quad \diagdown \\
 \text{R}^2 \quad \text{R}^1
 \end{array}$$

Entry	Ligand	Substrate R ¹	R ²	Solvent	t [min]	Conversion [%]	ee [%]
1	3a	NHAc	Ph	CF ₃ CH ₂ OH	40	100	27 (R)
2	3a	NHAc	Ph	CH ₂ Cl ₂	30	100	23 (R)
3	3a	NHAc	Ph	CH ₃ OH	400	100	22 (R)
4	3a	CH ₂ COOMe	H	CF ₃ CH ₂ OH	10	100	18 (S)
5	3a	CH ₂ COOMe	H	CH ₂ Cl ₂	1400	100	11 (S)
6	3a	CH ₂ COOMe	H	CH ₃ OH	300	100	12 (S)
7	3b	NHAc	Ph	CF ₃ CH ₂ OH	200	100	31 (R)
8	3b	NHAc	Ph	CH ₂ Cl ₂	60	100	71 (R)
9	3b	NHAc	Ph	CH ₃ OH	70	100	77 (R)
10	3b	CH ₂ COOMe	H	CF ₃ CH ₂ OH	60	100	57 (R)
11	3b	CH ₂ COOMe	H	CH ₂ Cl ₂	40	100	49 (R)
12	3b	CH ₂ COOMe	H	CH ₃ OH	45	100	76 (R)
13	4	NHAc	Ph	CF ₃ CH ₂ OH	25	100	13 (R)
14	4	NHAc	Ph	CH ₂ Cl ₂	7	100	56 (R)
15	4	NHAc	Ph	CH ₃ OH	2	100	90 (R)
16	4	CH ₂ COOMe	H	CF ₃ CH ₂ OH	4	100	61 (S)
17	4	CH ₂ COOMe	H	CH ₂ Cl ₂	8	100	87 (S)
18	4	CH ₂ COOMe	H	CH ₃ OH	2	100	58 (S)

^[a] For reaction conditions and analysis of products, see Table 1.

techniques. Solvents were dried and freshly distilled under argon before use. The 1,1,1,3,3,3-hexafluoro-2-propanol and 2-fluoroethanol were purchased from ABCR and Alfa Aesar, respectively. Syntheses of the phospholane ligands **1**, **3** and phosphepine ligands **2**, **4** were reported recently.^[8] ¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker Spectrometer AVANCE 500 and 300 (¹H: 500.13 MHz and 300.13 MHz; ¹³C: 125.8 MHz and 75.5 MHz; ³¹P: 162.0 MHz). Chemical shifts of ¹H, ¹³C and ³¹P NMR spectra are reported in ppm. The calibration of ¹H and ¹³C spectra was carried out on solvent signals [δ (CDCl₃) = 7.25 and 77.0]. The ³¹P chemical shifts are referenced to 85% H₃PO₄. The optical rotations were measured on a "gyromat-HP" instrument (Fa. Dr. Kernchen). Mass spectra were recorded on a MAT 95XP (Finnigan).

General Procedure for the Enantioselective Hydrogenation

All hydrogenation reactions were carried out under standard conditions: isothermal (25 °C) and isobaric (1 bar) conditions in an automatically registering hydrogenation device. Precatalysts were prepared *in situ* by mixing [Rh(COD)₂](BF₄) (1 equiv.) and chiral ligands (2 equivs.) under an argon atmosphere (catalyst loading S/C 50/1 or 100/1). Then the prochiral olefin (0.5 mmol) and the solvent (7.5 mL) were added and after changing of argon by hydrogen the hydrogenation was started. The conversion of the prochiral olefins was determined by GC. For the enantiomer ratio determinations GC columns with chiral stationary phases (lipodex E column) from Macherey–Nagel GmbH were used.

Acknowledgements

The authors are grateful to BASF AG (Ludwigshafen) for financial support of this work. We acknowledge valuable discussions with Prof. Dr. B. Breit (Freiburg). We thank Dr. C. Fischer and Mrs. S. Buchholz for the analysis of the chiral hydrogenation products.

References

- [1] For reviews, see: M. J. Wilkinson, P. W. N. M. van Leeuwen, J. N. H. Reek, *Org. Biomol. Chem.* **2005**, *3*, 2371–2383; S. J. Reyes, K. Burgess, *Chem. Soc. Rev.* **2006**, *35*, 416–423; A. W. Kleij, J. N. H. Reek, *Chem. Eur. J.* **2006**, *12*, 4218–4272.
- [2] X.-B. Jiang, L. Lefort, P. E. Goudriaan, A. H. M. de Vries, P. W. N. M. van Leeuwen, J. G. de Vries, J. N. H. Reek, *Angew. Chem.* **2006**, *118*, 1245–1249; *Angew. Chem. Int. Ed.* **2006**, *45*, 1223–1227; J. M. Takacs, D. S. Reddy, S. A. Moteki, D. Wu, H. Palencia, *J. Am. Chem. Soc.* **2004**, *126*, 4494–4495; J. M. Atkins, S. A. Moteki, S. G. DiMaggio, J. M. Takacs, *Org. Lett.* **2006**, *8*, 2759–2762; L. K. Knight, Z. Freixa, P. W. N. M. van Leeuwen, J. N. H. Reek, *Organometallics* **2006**, *25*, 954–960.
- [3] D. E. Koshland, *Proc. Natl. Acad. Sci. USA* **1958**, *44*, 98–104; G. E. Schulz, *Faraday Discuss.* **1992**, *93*, 85–93; H. Pelletier, M. R. Sawaya, W. Wolffe, S. H. Wilson, J. Kraut, *Biochemistry* **1996**, *35*, 12742–12761; M. R. Sawaya, R. Prasad, S. H. Wilson, J. Kraut, H. Pelletier, *Biochemistry* **1997**, *36*, 11205–11215.

- [4] a) B. Breit, W. Seiche, *J. Am. Chem. Soc.* **2003**, *125*, 6608–6609; b) B. Breit, W. Seiche, *Pure Appl. Chem.* **2006**, *78*, 249–256; c) W. Seiche, A. Schuschkowski, B. Breit, *Adv. Synth. Catal.* **2005**, *347*, 1488–1494; d) T. Šmejkal, B. Breit, *Organometallics* **2007**, in press; DOI: 10.1002/ejoc.200600849; e) F. Chevallier, B. Breit, *Angew. Chem.* **2006**, *118*, 1629–1632; *Angew. Chem. Int. Ed.* **2006**, *45*, 1599–1602.
- [5] B. Breit, W. Seiche, *Angew. Chem.* **2005**, *117*, 1666–1669; *Angew. Chem. Int. Ed.* **2005**, *44*, 1640–1643; B. Breit, *Angew. Chem.* **2005**, *117*, 6976–6986; *Angew. Chem. Int. Ed.* **2005**, *44*, 6816–6825.
- [6] M. Weis, C. Walloch, W. Seiche, B. Breit, *J. Am. Chem. Soc.* **2006**, *128*, 4188–4189.
- [7] For a related concept, see: Y. Liu, C. A. Sandoval, Y. Yamaguchi, X. Zhang, Z. Wang, K. Kato, K. Ding, *J. Am. Chem. Soc.* **2006**, *128*, 14212–14213.
- [8] M.-N. Birkholz, N. V. Dubrovina, H. Jiao, D. Michalik, J. Holz, R. Paciello, B. Breit, A. Börner, *Chem. Eur. J.* **2007**, *13*, 5896–5907.
- [9] E_N^T values: a) C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358; b) For MFE: K. Sraidi, *These de Doctorat d'Etat*, Marrakech, **1986**; C. Laurence, M. Berthelot, J. Graton, in: *The Chemistry of Phenols*, (Ed.: Z. Rappoport), Wiley, Chichester, **2003**; pp 529–603; hydrogen bond acceptor (β) values: c) S. Spange, E. Vilsmeier, S. Adolph, A. Fährmann, *J. Phys. Org. Chem.* **1999**, *12*, 547–556; M. J. Kamlet, J. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887; C. Laurence, M. Berthelot, M. Helbert, K. Sraidi, *J. Phys. Chem.* **1989**, *93*, 3799–3802; M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1990**, 521–529.
- [10] ^{31}P NMR data measured for the same complex in CDCl_3 : $\delta = 54.5$ [dd, $J(^{31}\text{P},^{103}\text{Rh}) = 146$ Hz, $J(^{31}\text{P},^{31}\text{P}) = 36$ Hz]; $\delta = 50.7$ [dd, $J(^{31}\text{P},^{103}\text{Rh}) = 137$ Hz, $J(^{31}\text{P},^{31}\text{P}) = 36$ Hz].
- [11] a) L. Shi, X. Wang, C. A. Sandoval, M. Li, Q. Qi, Z. Li, K. Ding, *Angew. Chem.* **2006**, *118*, 4214–4218; *Angew. Chem. Int. Ed.* **2006**, *45*, 4108–4112; b) P. A. Duckmant, A. J. Blake, J. B. Love, *Inorg. Chem.* **2005**, *44*, 7708–7710.
- [12] Probably these polymeric complexes are responsible for the low reaction rates. Compare, for example, ref.^[11a] where such systems have been employed, but more drastic hydrogenation conditions are required.
- [13] For other beneficial applications of fluorinated alcohols in homogeneous catalysis, see: for review: I. A. Shuklov, N. V. Dubrovina, A. Börner, *Synthesis* **2007**, in press; a) Mukaiyama–Michael reaction: D. A. Evans, K. A. Scheidt, J. N. Johnston, M. C. Willis, *J. Am. Chem. Soc.* **2001**, *123*, 4480–4491; b) Oxidation: J.-P. Bégué, D. Bonnet-Delpon, B. Crousse, *Synlett* **2004**, 18–29; c) [4+2] cycloaddition: A. Saito, T. Ono, Y. Hanzawa, *J. Org. Chem.* **2006**, *71*, 6437–6443; in homogeneous catalytic hydrogenation, see, e.g.: d) H. Abe, H. Amii, K. Uneyama, *Org. Lett.* **2001**, *3*, 313–315; A. Suzuki, M. Mae, H. Amii, K. Uneyama, *J. Org. Chem.* **2004**, *69*, 5132–5134; e) N. V. Dubrovina, V. I. Tararov, A. Monsees, R. Kadyrov, C. Fischer, A. Börner, *Tetrahedron: Asymmetry* **2003**, *14*, 2739–2745; N. V. Dubrovina, V. I. Tararov, A. Monsees, A. Spannenberg, I. D. Kostas, A. Börner, *Tetrahedron: Asymmetry* **2005**, *16*, 3640–3649; f) Y. Hsiao, N. R. Rivera, T. Rosner, S. W. Krska, E. Njolito, F. Wang, Y. Sun, J. D. Armstrong, E. J. J. Grabowski, R. D. Tillye, F. Spindler, C. Malan, *J. Am. Chem. Soc.* **2004**, *126*, 9918–9919; g) W. Zhang, X. Zhang, *J. Org. Chem.* **2007**, *72*, 1020–1023; h) palladium-catalyzed polymerization: A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, B. Milani, S. Gladiali, C. Carfagna, B. Binotti, S. Bronco, T. Gragnoli, *J. Organomet. Chem.* **2005**, *690*, 2106–2120; C. Bianchini, A. Meli, W. Oberhauser, A. M. Segarra, C. Claver, E. J. Garcia Suarez, *J. Mol. Catal. A: Chem.* **2007**, *265*, 292–305.