A (Figure 4). Thus, [**A**-**1**] is stabilized by both π–π and π–cation interactions. Furthermore, the binding of the guest would displace the water molecules in the cavity of **A**, thus providing a favorable entropic gain in [**A**-**1**].

In conclusion, we report an original example of adaptive host–guest systems which employs mutually induced fit between the conformationally flexible host **A** and guests **1**–**3**. Both the host and the guests adapted to each other and selected the higher energy but correct geometric conformers so that the guest could fit favorably into the cavity of the host to give ditopic binding. While mutually induced fit has been demonstrated mostly in biological macromolecules interactions, that is, in protein/DNA,[15] protein/RNA,[16] protein/tRNA complexes,[17] it has been recently depicted within a neocarzinostatin–chromophore/DNA complex.[18] Recent development in drug design has considered mutual adaptability between a ligand and a receptor as a key element in molecular recognition[19] and has prompted the outlining of the "relaxed-complex" method as a novel dynamic computational model to take into account the flexibility of receptors.[20] Therefore, our system represents an original example of adaptive supramolecular biomimetic chemistry.

Experimental Section

General: NMR spectra were recorded on a Bruker VPC 300 spectrophotometer unless otherwise mentioned. Solutions of complexes for NMR analysis were prepared in 0.1M deuterated phosphate buffer at pD 7.3 and 0.4. The molecular modeling study was performed by using Sybyl 6.8 on a Silicon Graphics Octane 2XR10000 station.

NMR titration: Experiments were carried out by keeping the concentration of guest (**1**–**3**) constant while varying that of the host (**A**) from 0.1 equiv to 10 equiv. Association constants K_A of the complexes were calculated with a nonlinear least-squares method.[9]

2D NMR analysis: Solutions for 2D NMR analysis were prepared with 20 mM of **1** and 40 mM of the host, which ensured over 99% complex formation between the guest and the host. 2D NMR spectra were recorded by using a NOESY sequence from Bruker (Noesyprtp) and a mixing time of 400 ms. Experiments were performed on **1**, [**A**-**1**], and the complex of *p*-sulfonated calix[4]arene with **1**.

Molecular modeling studies: The starting structure **1** was constructed from the coordinates of the crystal structure of an analogue.[6b] For **A**, two crystal structures of calix[8]arene (Dovhif[13] and Foztix[14]) were used as starting points to construct the structure and led to the pleated loop conformation and the pinched conformation, respectively. For the complex [**A**-**1**], **1** was manually docked with each conformer of **A**. All the starting structures of **1**, **A**, and [**A**-**1**] were optimized by a molecular mechanics algorithm using the Tripos force field with a convergence criterion of 0.01 kcal mol^{-1}. The electrostatic component was applied by means of the Gasteiger–Hückel charges and a dielectric function equal to 1.

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New Ferrocenyl Ligands with Broad Applications in Asymmetric Catalysis**

Matthias Lotz, Kurt Polborn, and Paul Knochel*

The development of new ligands for asymmetric catalysis is an highly active field of research.[1] Although many chiral ligands have been prepared, only a few, such as binaphthyl-,[2] salen-,[3] pybox-,[4] and DuPHOS-type[5] ligands have found broad applications in various asymmetric reactions. The ferrocenyl unit has proven to allow excellent spatial recognition,[6] and we recently reported new ferrocenyl diphosphanes of type **1** (taniaphos),[7] which gave excellent results in

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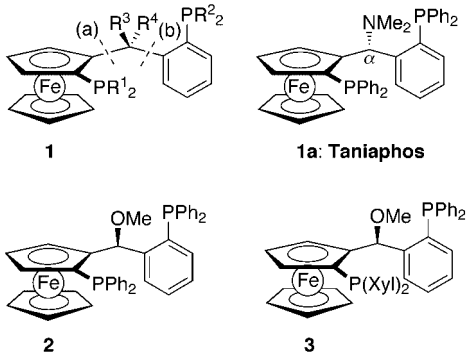
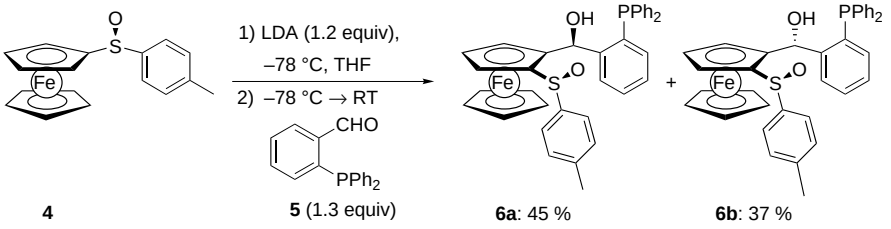


Ru-catalyzed asymmetric hydrogenations of 1,3-dicarbonyl compounds.[8,9]

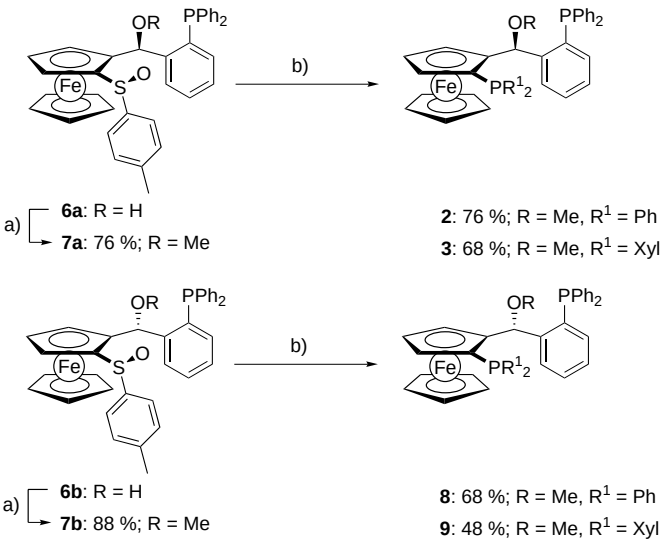
Although the original synthesis (retrosynthetic cleavage (a)) was concise, high-yielding, and stereoselective, it suffered from two major drawbacks: 1) it did not allow independent variation of the phosphane substituents R^1 and R^2, 2) it was not possible to prepare ligands with $R^3 \neq H$—only the nature of R^4 could be altered. This hampered the full exploitation of the modular character of ligands **1**. Herein we report a new preparation of ligands **2** and **3** (involving the retrosynthetic bond cleavage (b)) which solves these two previous synthetic limitations. The new ligands **2** and **3**, which bear a methoxy substituent instead of a hydrogen atom at the α position, provided high enantioselectivities in many asymmetric transformations.[10] Thus, the reaction of lithiated ferrocenyl sulfoxide (*S*)-**4** (first used by Kagan and co-workers[11]) with 2-diphenylphosphanylbenzaldehyde (**5**) furnished the two diastereomeric alcohols (S_p,α*S*)-**6a** and (S_p,α*R*)-**6b** (55:45) in 82% yield (Scheme 1). The diastereomers were readily separated by column chromatography.



Scheme 1. Preparation of the diastereomeric ferrocenyl alcohols **6a** and **6b**. LDA = lithium diisopropylamide.

X-ray crystallographic analysis[12] proved that the major diastereomer (S_p,α*S*)-**6a** has the opposite configuration at the α-position compared to taniaphos (**1a**), whereas the second diastereomer (S_p,α*R*)-**6b** has the same configuration as ligand **1a**. Both intermediate ferrocenyl alcohols **6a**,**b** can be converted readily into the corresponding methyl ethers **7a**–**b** in 76–88% yield by deprotonation and methylation (Scheme 2). Treatment of **7a**–**b** with *t*BuLi (2.0 equiv) in THF at −78 °C (10 min), followed by the addition of chlorodiphenylphosphane or chloro[bis(3,5-dimethylphenyl)]phosphane, provides the desired diphosphanes **2**, **3**, **8**, and **9** in 48–76% yield.[13]

As mentioned above, the new diphosphanes **2** and **3**, which are epimeric to taniaphos (**1a**) at the α position, lead to high



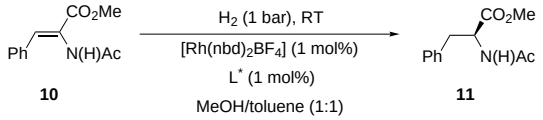
Scheme 2. Reagents and conditions: a) KH (1.3 equiv), THF, 0 °C; then MeI (1.1 equiv), 0 °C→RT; b) *t*BuLi (2.0 equiv), THF, −78 °C, 10 min; then $ClPPh_2$ or $ClP(Xyl)_2$ (3.5 equiv), −78 °C→RT.

enantioselectivities in a wide range of asymmetric reactions. First, we compared all the new ligands in the Rh-catalyzed hydrogenation of (*Z*)-α-methylacetamidocinnamate (**10**).[8,14]

Thus, treatment of **10** with hydrogen (1 bar, room temperature, 0.5–1.5 h) in the presence of $[Rh(nbd)_2BF_4]$ (nbd = norbornadiene) (1 mol%) and the ligand (1 mol%) in methanol/toluene (1:1) leads to (*S*)-*N*-acetyl phenylalanine methyl ester (**11**) in quantitative yield and with high enantioselectivity. Whereas taniaphos (**1a**) gives the (*R*)-*N*-acetyl phenylalanine methyl ester (**11**) in 95% *ee*, all the new catalysts **2**, **3**, **8**, and **9** furnish the (*S*)-*N*-acetyl phenylalanine methyl ester. This behavior is general and was observed in all hydrogenation reactions. Ligands **2** and **3** give the highest enantioselectivities (99% *ee*), thus showing the importance of the configuration at the α position (Table 1).

Similarly, the Rh-catalyzed hydrogenation of dimethyl itaconate[8,14,15] (**13**) to (*R*)-methyl succinic acid dimethyl ester (**14**) proceeds with excellent enantioselec-

Table 1. Rh-catalyzed asymmetric hydrogenation of **10** to (*S*)-*N*-acetyl phenylalanine methyl ester (**11**).



Entry	Ligand	*t* [h]	Conversion [%]	*ee* [%][a]
1	**2**	1.5	100	99 (*S*)
2	**3**	1.5	100	99 (*S*)
3	**8**	2	100	94 (*S*)
4	**9**	1.5	100	92 (*S*)
5	**1a**	0.5	100	95 (*R*)

[a] Determined by means of chiral GC (Chirasil-*L*-Val column). The absolute stereochemistry was established by comparison with literature data.[5b]

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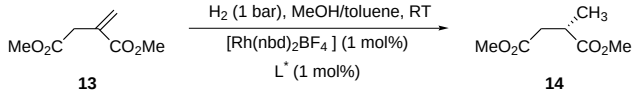
tivity in the presence of ligand **2** (98% *ee*), which again gives superior results than do the ligands **8** and **1a** (Table 2).

Table 2. Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate (**13**) to (*R*)-methyl succinic acid dimethyl ester (**14**).



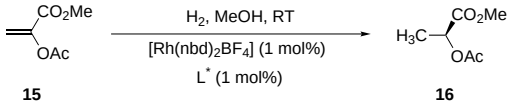
13 **14**

Entry	Ligand	*p* [bar]	*t* [h]	Conversion [%]	*ee* [%][a]
1	**2**	1	0.5	100	98 (*R*)
2	**3**	1	1	100	90 (*R*)
3	**8**	1	2.5	100	95 (*R*)
4[b]	**1a**	1	14	100	91 (*S*)

[a] Determined by chiral HPLC (Daicel Chiracel OD column). The absolute stereochemistry was established by comparison with literature data.[14] [b] Reaction was performed in MeOH.

Whereas the taniaphos ligands with S_p,α*R* configuration display a low reactivity and moderate enantioselectivity in the asymmetric hydrogenation of α-acetoxy acrylic acid esters such as **15**[5a,15] (Table 3; see ligands **1a**, **8**, **9**), the new epimeric diphosphanes **2** and **3** (S_p,α*S*) have a significantly higher catalytic activity (the reaction proceeds at 1 bar compared to 5–10 bar with ligands **1a**, **8**, **9**) and lead to excellent enantioselectivities (99% *ee*).

Table 3. Asymmetric hydrogenation of α-acetoxy acrylic acid methyl ester (**15**).



15 **16**

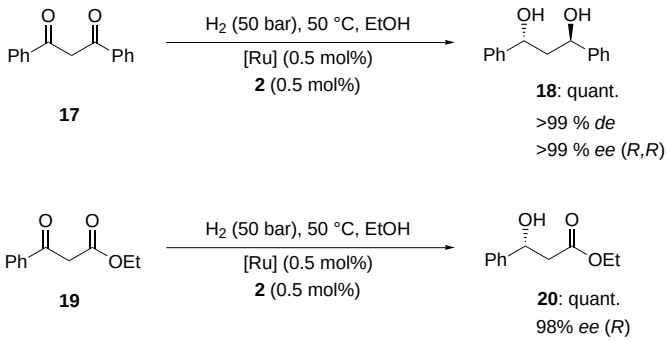
Entry	Ligand	*p* [bar]	*t* [h]	Conversion [%]	*ee* [%][a]
1	**2**	1	20	100	98 (*S*)
2	**3**	1	20	100	99 (*S*)
3	**8**	1	20	40	–[b]
4	**8**	10	20	100	80 (*S*)
5	**9**	10	20	100	78 (*S*)
6	**1a**	5	22	95	72 (*R*)

[a] Determined by chiral HPLC (Daicel Chiracel OD-H column). The absolute stereochemistry was established by comparison with literature data.[16] [b] The *ee* value was not determined.

Remarkable enantioselectivity is also observed in the Ru-catalyzed hydrogenation of dibenzoylmethane (**17**), which furnishes only the *anti*-(1*R*,3*R*)-diol **18** in >99% *ee* and >99% *de* (Scheme 3).

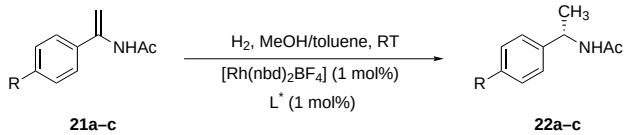
Similarly, the Ru-catalyzed hydrogenation of ethyl 3-phenyl-3-oxopropionate (**19**) provides the aldol product **20** with 98% *ee*. These hydrogenation reactions were performed under the standard conditions: $[Ru(cod)(C_4H_7)_2]/HBr$[17] (cod = cycloocta-1,5-diene) (0.5 mol%), ligand **2** (0.5 mol%) in ethanol at 50°C and under 50 bar H_2.

Finally, we examined the Rh-catalyzed hydrogenation of aryl-substituted enamides[18] of type **21**. The ligands **2** and **3** turned out to be very active in this reaction and provided excellent enantioselectivities of up to 97% *ee* (Table 4). Remarkably, these hydrogenations occur at 1 bar H_2 with complete conversion within 1.5–15 h at 25°C.



Scheme 3. Enantioselective hydrogenation of dibenzoylmethane (**17**) and ethyl 3-phenyl-3-oxopropionate (**19**).

Table 4. Rh-catalyzed asymmetric hydrogenation of enamides **21** to amides **22**.



21a–c **22a–c**

Entry	Substrate	Ligand	R	*p* [bar]	*t* [h]	Product	*ee* [%][a,b]
1	**21a**	**2**	H	1	15	**22a**	96 (*S*)
2	**21b**	**2**	Br	1	6	**22b**	97 (*S*)
3	**21a**	**3**	H	1	1.5	**22a**	92 (*S*)
4	**21b**	**3**	Br	1	1.5	**22b**	93 (*S*)
5	**21c**	**3**	Me	1	1.5	**22c**	95 (*S*)

[a] Determined by chiral HPLC (Daicel Chiracel OD column). [b] Determined by chiral GC (columns: Chirasil-L-Val, Chirasil-Dex CD, Chirasil-Dex CB). The absolute stereochemistry was established by comparison with literature data.[18]

We assume that the high activity and excellent enantioselectivity of ligands **2** and **3** in asymmetric catalysis is a result of the *S* configuration at the carbon atom that bears the methoxy group. This configuration may lead to a shielding of the upper half of the diphosphane–metal complex, thus forcing the asymmetric reaction to occur from the bottom face.

Although a rational explanation of the observed enantioselectivities is difficult at this point in time, the short, modular synthesis of the new ligands (S_p,α*S* configuration) and the remarkably high enantioselectivities obtained in asymmetric catalysis, combine to provide a new family of powerful and broadly applicable chiral ligands. Extension of the field of application of these ligands in asymmetric catalysis is currently underway.

Experimental Section

Enantioselective hydrogenation of **21a**: $[Rh(nbd)_2BF_4]$ (2.8 mg, 1 mol%) and ligand **2** (5.0 mg, 1 mol%) were dissolved in MeOH/toluene (2 mL) in a 25-mL Schlenk tube under argon. After 20 min, a solution of **21a** (120 mg, 0.74 mmol) in MeOH (5 mL) was added. The Schlenk tube was connected to a hydrogen balloon and the inert atmosphere was replaced by hydrogen. After complete conversion (monitored by TLC) the solvent was removed, and the crude reaction mixture was filtered through a short silica-gel column with Et_2O as eluent. After evaporation of the solvent (*S*)-**22a** was obtained in quantitative yield (122 mg, 0.74 mmol) as a yellowish solid (96% *ee*).

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[12] CCDC 189275 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] A typical procedure for the synthesis of diphosphane **2** is described in the Supporting Information.

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A Remarkable 14-Nuclear $Re^{V}_{8}Ag^{I}_{6}$ Coordination Oligomer Derived from a 2D $(Re^{V}_{2}Ag^{I}_{2})_n$ Coordination Polymer with D-Penicillaminate

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There has been considerable interest in the design and creation of metallo-supramolecular systems that exhibit unique structural and chemical properties.[1] In many cases, metallo-supramolecular structures have been constructed from organic multidentate ligands and metal ions through self-assembly processes. Our synthetic strategy involves the use of octahedral metal complexes containing relatively simple thiolate ligands, such as 2-aminoethanethiolate (aet), L-cysteinate (L-cys), and D-penicillaminate (D-pen; D-H_2pen = D-penicillamine), as building blocks that are aggregated by forming S-bridged structures with metal ions.[2–5] This method allows the construction of well-organized heterometallic aggregates which have several chiral centers by a systematic variation and combination of metal ions with different coordination geometries. For example, a number of chiral S-bridged aggregates, which include $Co^{III}_4Pd^{II}_2M^{I}_2$ octanuclear metallacycles $[M^{I}_2\{Pd^{II}[Co^{III}(aet)_3]_2\}_2]^{6+}$ (M = Ag, Au),[2e] have been prepared just from $[Co^{III}(aet)_3]$ and appropriate metal ions.[2]

While it has been established that thiolato groups coordinated to an M^{II} or M^{III} metal center have the ability to bind to a second metal ion to form S-bridged structures,[2–6] the coordinating ability of thiolato groups bound to a metal center with a higher oxidation state has not been widely investigated.[7] In fact, S-bridged heterometallic aggregates based on

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