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Modular chiral ligands: the profiling of the Mandyphos and Taniaphos ligand families

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Abstract—A set of 11 ferrocenyl based diphosphine ligands (eight Mandyphos and three Taniaphos) was tested in more than 150 experiments using 20 test reactions. For the assessment of new ligands, a two-pronged strategy was developed consisting of a basic and an extended profiling. The basic profiling showed that the choice of the substituents at the P atoms has a significant effect on the catalyst performance. In the extended profiling it was confirmed that the Mandyphos ligands, in particular **M4** with two bis(3,5-dimethyl-4-methoxyphenyl)phosphino groups, and the Taniaphos ligands, especially the all-phenyl derivative **T1**, showed good to outstanding performances in the hydrogenation of selected α- and β-enamides, acrylic acid derivatives, itaconates, β-ketoesters and 1,3-diketones yielding the corresponding products with up to 99% ee and at substrate/catalyst ratios up to 25,000.

1. Introduction

The most effective enantioselective catalysts are complexes consisting of a central metal ion and one or more chiral ligands (see Fig. 1).[1] There is no doubt that the choice of a specific metal–ligand combination essentially determines what transformation a complex is able to catalyze selectively. For hydrogenation reactions, the most active and versatile catalysts are low valent Rh, Ru and Ir complexes with tertiary phosphorus ligands in which the chiral element is either the backbone or sometimes the coordinating phosphine.[2,3] An analysis of the results reported so far shows two somewhat contradictory tendencies. On the one hand, relatively high catalyst specificity is observed, that is, a small change in either ligand or substrate structure often has a strong effect on the catalytic performance (ee, ton, tof). On the other hand, there are a number of ligand families, which are more likely to give better performances than others. For these, Jacobsen has coined the term 'privileged ligands' (for selected examples see Fig. 1).

If we want to make catalytic enantioselective hydrogenation a valuable tool for the synthetic chemist, these observations have two consequences: (i) a large variety of ligands has to be designed and prepared, and (ii) their catalytic profiles, that is, the suitability to catalyze specific transformations, should be well known. Even if one applies certain restricting design principles there is still an almost unlimited number of potential ligands, which should be tested for interesting reactions. Obviously, a compromise has to be reached between the benefits of structural diversity and the costs and time involved preparing and testing a large number of ligands. Solvias decided on the following concept: Concentrate on a relatively small number of privileged ligands families, which are highly modular and easily tuned both sterically and electronically with a reasonable amount of synthetic effort. For each ligand family we synthesized various members with a sufficient electronic and steric diversity and tested each in a number of test reactions to obtain a good performance profile for each ligand. This concept has already been implemented successfully for the Josiphos ligand family, albeit with a limited number of test reactions.[4]

Herein we report on a systematic investigation of the catalytic properties of the Mandyphos and Taniaphos ligand families (see Fig. 2) first prepared by Knochel

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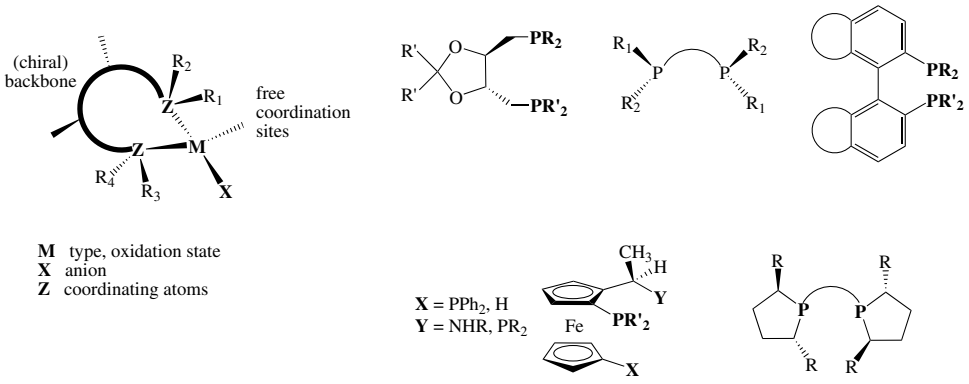

Figure 1. Design elements for chiral metal complexes and selected privileged ligand backbones for enantioselective hydrogenation.

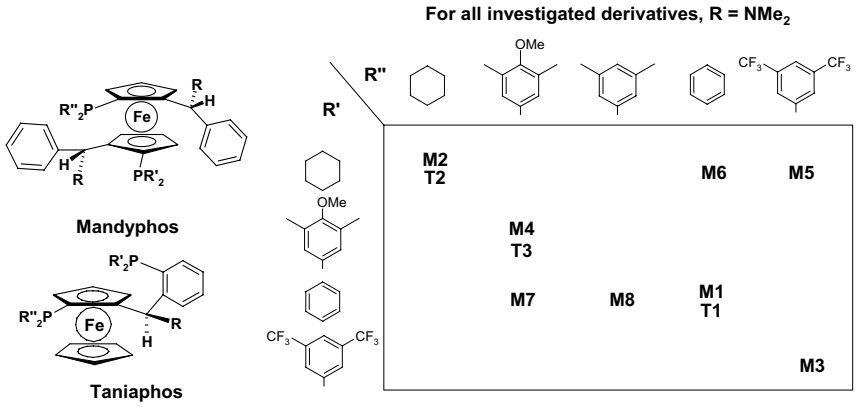

Figure 2. Generic structures of the Mandyphos® **M** and Taniaphos® **T** ligand families and abbreviations used for tested ligands. As a general rule, ligand basicity decreases going to the right and down.

in collaboration with Degussa[5,6] and now being commercialized by Solvias for Umicore. The Mandyphos diphosphines[5] have a C_2-symmetrical backbone with structural motifs related to ppfa[7] (see Fig. 3). Herein, several C_1 (or pseudoC_2)-symmetrical derivatives (R′≠R″) were also prepared (**M5**–**M8**). The Taniaphos family[6] has a C_1-symmetrical backbone and forms eight-membered metallacycles similar to the Walphos ligands (Fig. 3), independently developed around the same time by Weissensteiner et al.[8] In the original publications, it was shown that for both ligand types, varying the R substituent on the side chain had a strong effect on the ee, whereas the effect of R′ and R″ on phosphorus was not investigated systematically. Herein we show that the nature of R′ and R″ has also a very strong effect on the catalytic performance and that this can be used to tailor the ligand to a particular transformation with relatively little synthetic effort.

2. Results and discussion

2.1. Basic ligand profiling

The profiling of a new ligand is the most important aspect when assessing its usefulness for practical applications. To do this as effectively as possible we have developed a two-pronged strategy. For the first assessment of a ligand's potential and for comparisons with literature results, we carried out several standard test reactions with C=C, C=N and C=O double bonds[2] (see Fig. 4) under standard reaction conditions (see Table 1). Depending on the results of this so-called *basic profiling* some or all ligands would then be tested either on additional, more demanding test substrates or under more demanding reaction conditions in order to assess the potential of the ligand for industrial problems (this we call *extended profiling*).

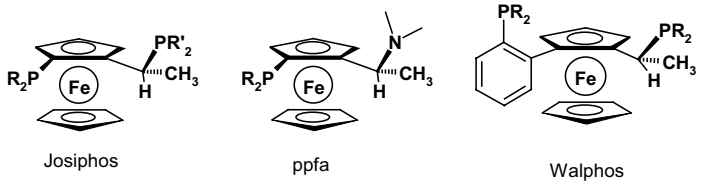

Figure 3. Ferrocene based phosphine ligands with similar structural motifs.

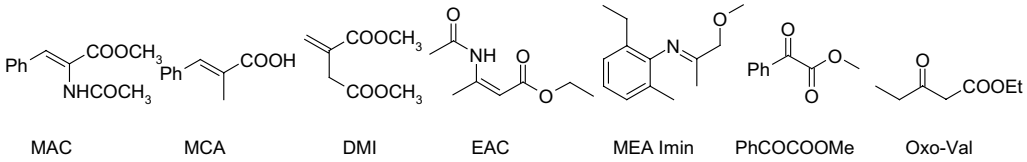

Figure 4. Structures and abbreviations of standard test substrates used in the basic profiling.

Table 1. Standard reaction conditions for basic profiling

Substrate (mmol)	Precursor	Solvent (mL)	*s/c*	*p* (bar)	*T* (°C)	*t* (h)	Additive
MAC, MCA, DMI (2.53)	$[Rh(nbd)_2]BF_4$	MeOH (10)	200	1[a]	25	1	
EAC (1.265)	$[Rh(nbd)_2]BF_4$	EtOH (9.5)	100	1	25	1	CF_3CH_2OH (0.5 mL)
MEA-Imine (12.65)	$[Ir(COD)Cl]_2$	Toluene (10)	100	80	25	16	TBAI (4.8 mg), CF_3COOH (30 μL)
PhCOCOOMe (2.53)	$[Rh(nbd)Cl]_2$	Toluene (10)	200	80	25	16	
Oxo-Val (2.53)	$[RuI_2(p\text{-cymene})]_2$	EtOH (10)	200	80	80	16	1 M HCl (60 μL)

[a] MCA at 5 bar.

The results for the basic profiling of the Mandyphos and Taniaphos families are summarized in Figures 5–7. As already observed in the initial publications,[5,6] the two ligand families have quite different performance profiles. Without going into detail, the following trends merit comments:

- Most Mandyphos ligands showed good to excellent ees and low to good tofs for MAC and MCA but low to mediocre ees for all other test substrates. In particular, catalyst Rh-**M4** hydrogenated MAC with >99.5% ee and a very high rate. While the good performance for MAC were expected because of already known results,[5] it is not clear why DMI is hydrogenated with such low ees.
- Taniaphos exhibited good to very good ees for MAC, DMI, EAC and Oxo-Val and low to mediocre ees for all other test substrates. **T3** deserves special mention with ees between 92% and >99.5%. Activities were high for the first two and medium to low for the other substrates. While good ees for MAC and DMI have already been described,[6] the good enantioselectivity of Taniaphos for EAC and especially for the Ru catalyzed hydrogenation of Oxo-Val was unexpected.

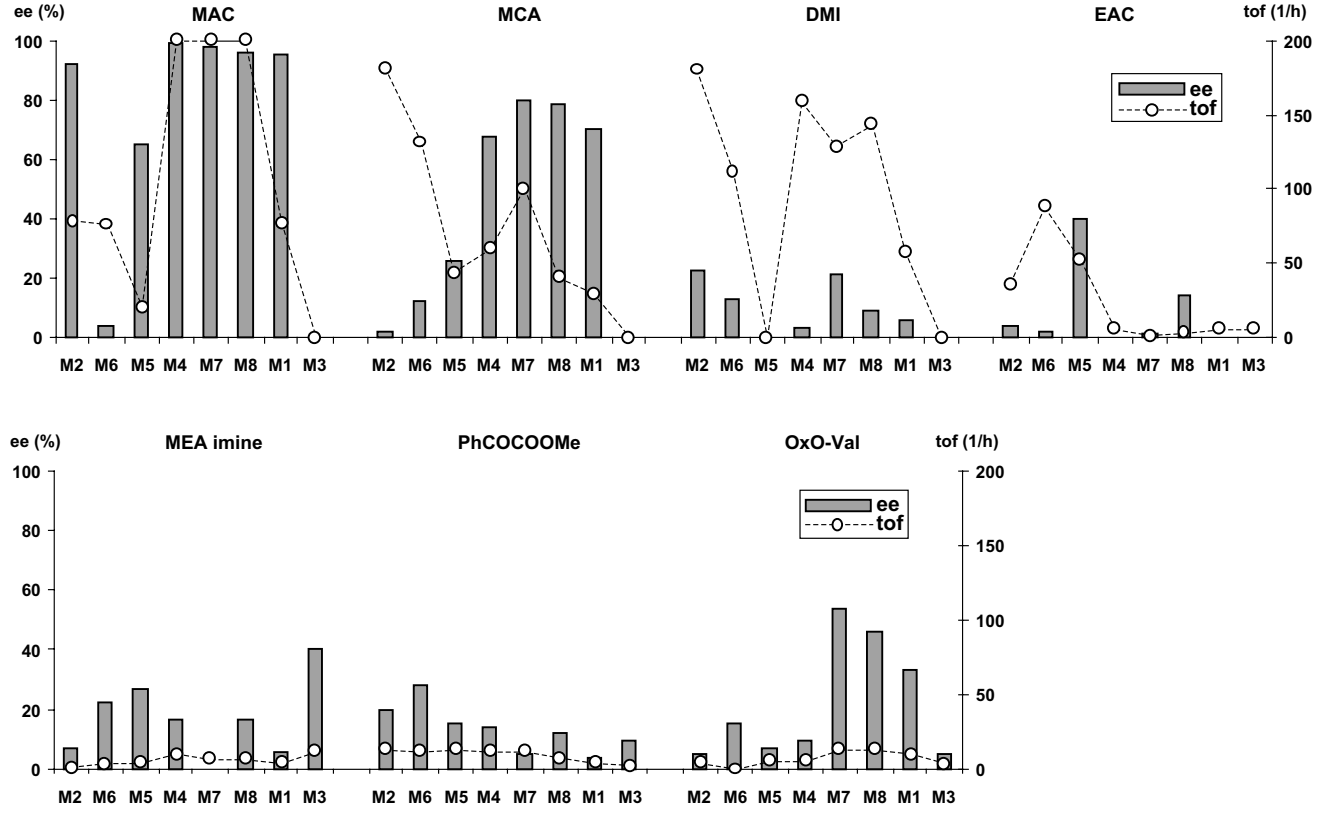

Figure 5. Basic profiling of Mandyphos; ee and tof for eight ligands and eight test substrates. Ligands ordered according to decreasing basicity (Cy > MeOXy > Xyl > Ph > CF_3Xyl).

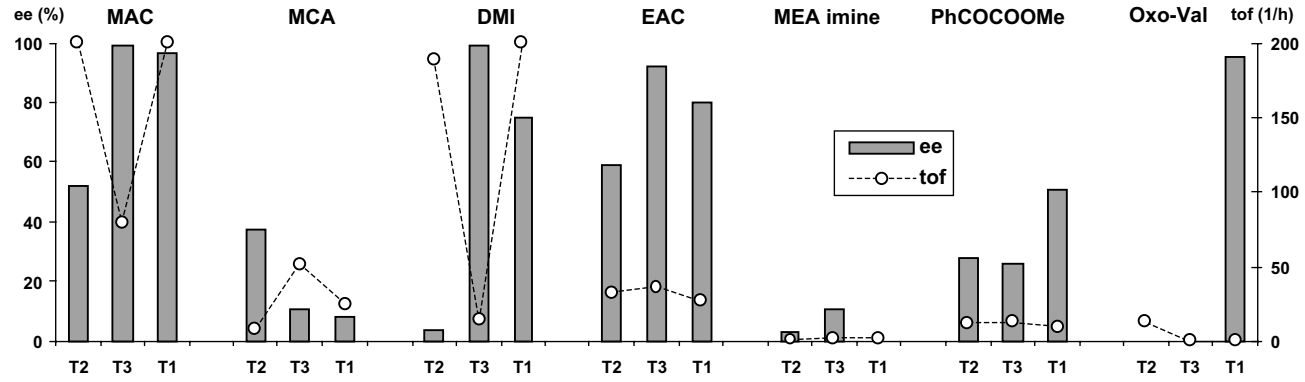

Figure 6. Basic profiling of Taniaphos; ee and tof for three ligands and eight test substrates. Ligands ordered according to decreasing basicity (Cy > MeOXyl > Ph).

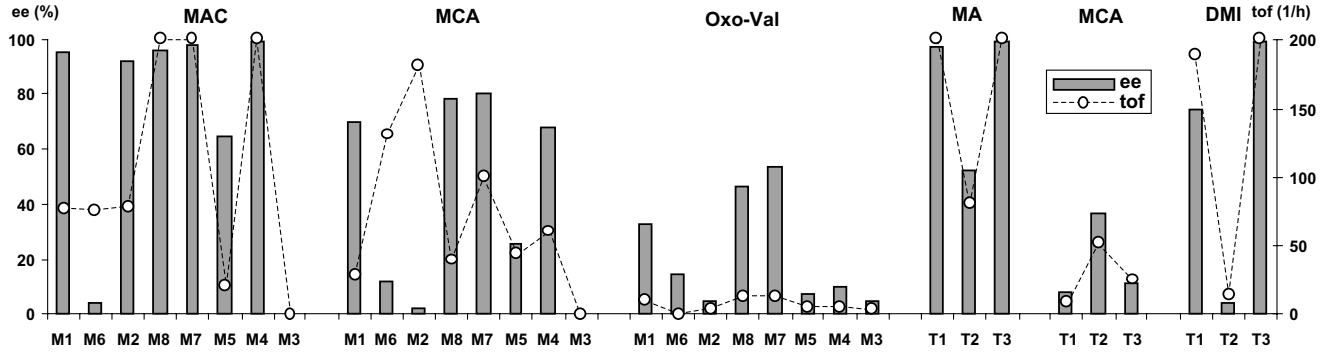

Figure 7. Ee and tof for Mandyphos and Taniaphos for selected test substrates. Ligands ordered according to increasing size (Ph < Cy < Xyl ~ MeO-Xyl ~ CF_3Xyl).

- For all test substrates and for both ligand families, the nature of the PR_2 groups had a significant influence on both the ee and tof. While there is no unequivocal correlation, a comparison of the selectivity patterns depicted in Figures 5–7 shows that it is the electronic property of the phosphine group (see Figs. 5 and 6) rather than its size (see Fig. 7), which has a systematic effect on the catalytic properties of the resulting complexes.
- With very few exceptions, relatively electron rich all-aryl substituted derivatives (Ph, Xyl, MeOXyl) gave the best performances for both ligand families. Ligands containing PCy_2 and $P(CF_3Xyl)_2$ groups in general gave moderate to very low ees and tofs. Except for MCA, EAC and Oxo-Val (low ees), symmetrically substituted Mandyphos derivatives usually showed a somewhat better performance than comparable unsymmetrical derivatives.

2.2. Extended ligand profiling

Based on these screening results, it was decided to select **M4** and **T1** for extended profiling with the following goals:

M4 *Technical performance*: Optimize the catalytic performance (ee, ton, tof) for MAC.

Scope: Study the effect of structural variations of MAC and MCA and investigate the hydrogenation of selected α-keto esters (see Fig. 8 and Table 2).

T1 *Scope*: Study the effect of structural variations of MAC, EAC and Oxo-Val and investigate the hydrogenation of selected α-keto esters, unsaturated acids and a hydrazone (see Fig. 8 and Table 3).

Furthermore, in some cases, pressure effects were investigated and for several substrates, both Rh and Ru catalysts were tested.

Comments on the performance of **M4** listed in Table 2

- MAC can be hydrogenated with industrially useful results: At 1 bar ee > 98%, tofs > 7500 h^{-1} and tons > 20,000 were achieved. The ee slightly dropped at higher *s/c* ratios and values >20,000 led to incomplete conversions (here the purity of the starting material starts becoming a critical issue). Increasing the temperature to 35 °C or the pressure to 5 bar led to a decrease in ee of ca. 1%. Compared to parent ligand **M1**, modified **M4** clearly has superior enantioselectivity and activity.
- The hydrogenation of dehydroamino acid derivatives with Rh-**M4** turned out to be quite sensitive to substrate structure. While ACA, the correspond-

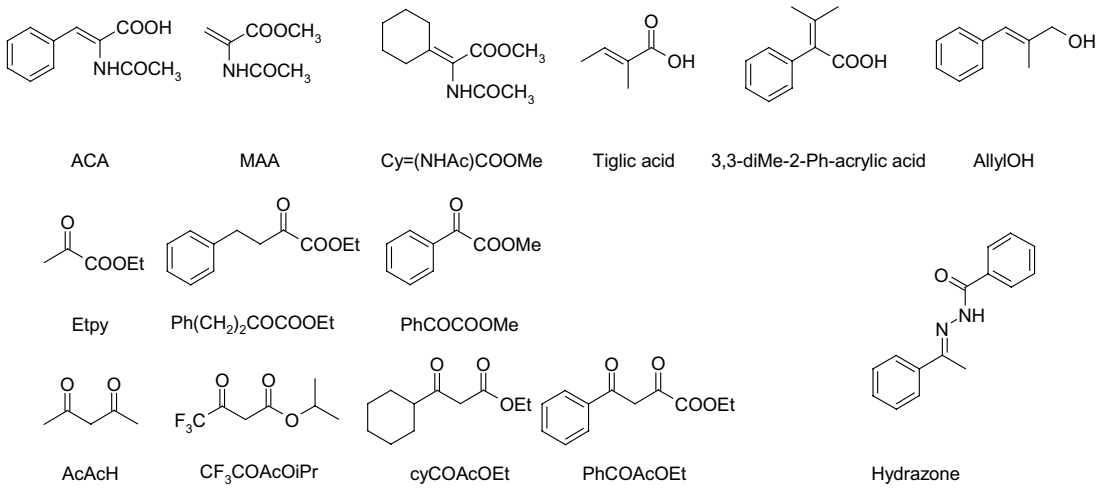

Figure 8. Structures and abbreviations of test substrates used in the extended profiling: dehydroamino acid derivatives, unsaturated acids, allylic alcohol, α-keto esters, β-functionalized ketones, hydrazone.

Table 2. Best results for enamides, activated olefins and α-keto esters with Mandyphos **M4** in the extended profiling

Substrate	Metal[a]	*p* (bar)	*t* (h)	Ee (%)	Tof (h^{-1})	Comments
MAC	Rh	1	20	97.6	50	ligand **M1**, *s/c* 1000
MAC	Rh	1	1.3	98	7692	*s/c* 10,000, 35 °C; ee 99% at 25 °C
MAC	Rh	1	7	98.6	2857	*s/c* 20,000
ACA	Rh	5	17.5	95	11	Ee 59% for Ru
MAA	Rh	1	1	95	200	
Cy=(NHAc)COOMe	Rh	1	20	37	10	
MCA	Rh	50	94	80	2	Ee 72% for Ru
Tiglic acid	Ru	5	18	97	11	Ee 76% for Rh
DiMe–Ph–acrylic acid	Rh	5	17	58	9[b]	No reaction with Ru
AllylOH	Rh	5	18	72	10[b]	No reaction with Ru
Etpy	Ru	50	21	69	5.2[b]	Solvent EtOH
$Ph(CH_2)_2COCOOEt$	Ru	50	18	88	10[b]	Solvent EtOH
PhCOCOOMe	Ru	50	22	66	5.4[b]	

Reaction conditions: *s/c* 200, 25 °C.
[a] Rh $[Rh(nbd)_2]BF_4$; Ru $[RuI_2(p\text{-cymene})]_2$.
[b] Incomplete conversion.

Table 3. Best results for enamides, activated olefins, α- and β-keto esters and a hydrazone with Taniaphos **T1** in the extended profiling

Substrate	Metal[a]	*p* (bar)	*t* (h)	Ee (%)	Tof (h^{-1})	Comments
MAC	Rh	5	22	96	9	Ee 97% at 1 bar
MAA	Rh	1	20	98	10	
Cy=(NHAc)COOMe	Rh	5	20	0.5	10	
MCA	Rh	50	20	10	10	
Tiglic acid	Ru	50	18	38	8[b]	Ee 32% at 5 bar
DiMe–Ph–acrylic acid	Rh	5	17	66	8[b]	
AllylOH	Rh	5	18	55	10[b]	
$Ph(CH_2)_2COCOOEt$	Ru	50	20	41	9	Solvent EtOH
AcAcH	Ru	80	16	99.5	13	Additive 1 M HCl; dl/meso 97
CF_3 COAcO*i*Pr	Ru	10	20	84	10	Solvent *i*PrOH, 1 M HCl
cyCOAcOEt	Ru	80	18	81	11	Solvent EtOH, 1 M HCl
PhCOAcOEt	Ru	80	16	94	13	Solvent EtOH, 1 M HCl
AcAcOEt[c]	Ru	80	20	79	1200	Solvent EtOH, 1 M HCl
Hydrazone	Rh	5	20	33	1	Conversion 11%

Reaction conditions: MeOH, *s/c* 200, 25 °C.
[a] Rh $[Rh(nbd)_2]BF_4$; Ru $[RuI_2(p\text{-cymene})]_2$.
[b] Incomplete conversion.
[c] *s/c* 25,000.

ing free acid, and MAA (no phenyl group) were hydrogenated with significantly lower but still very good enantioselectivities, the tetra substituted Cy=(NHAc)COOMe only gave 37% ee. This is in contrast to the Rh-Duphos catalysts, which are less sensitive to the degree of substitution and configuration of the C=C bond.[2]

- An even stronger structure sensitivity was found for α,β-unsaturated olefins. An unprecedented performance was observed for the Ru catalyzed hydrogenation of tiglic acid (ee 97%, full conversion). The best results for MCA and 3,3-dimethyl- 2-phenyl-acrylic acid were obtained with Rh catalysts with ees of 80% and 58%, respectively, and allylOH reduced with 72% ee.
- Acceptable results were also obtained for α-keto esters. The best enantiomeric excess was obtained for the hydrogenation of the commercially interesting HPB-keto ester ($Ph(CH_2)_2COCOOEt$, 88% ee) while ees of up to 69% ee and 66% ee were achieved for etpy and PhCOCOOMe, respectively.

Comments on the performance of **T1** listed in Table 3

- Taniaphos ligand **T1** is suitable for the Rh catalyzed hydrogenation of selected enamides and is very efficient for the Ru catalyzed hydrogenation of β-diketones and β-keto esters. The results for the other tested substrate classes confirm the initial tests and are not useful for preparative application.
- The most outstanding result was obtained in the hydrogenation of acetylacetone yielding (2*R*,4*R*)-pentanediol with 99.5% ee with an excellent diastereoselectivity of 97.4:1 (dl:meso). At this small scale, Ru-SL is an alternative for the Ru-Binap or R–MeObiphep catalysts; the potential for large scale application has yet to be investigated.
- AcAcOEt could be hydrogenated with Ru-**T1** on a 154 mmol scale with an *s/c* ratio of 25,000 with complete conversion after 20 h, but with only 78.8% ee; significantly lower than the 96% ee obtained at *s/c* 100.[5] The reasons for this drop in enantioselectivity is not clear and should be studied in more detail.
- Other β-keto esters were also hydrogenated with good to high ees, whereas α-keto esters or hydrazones seemed to be unsuitable substrates for this Ru catalyst.
- A broad selection of alkenes was studied but only di and trisubstituted α-enamides gave high enantioselectivities. All other tested C=C substrates were hydrogenated with medium to very low ees. The performance of this catalyst for α-enamides is strongly dependent on the degree of substitution at the C=C bond.

3. Conclusions

The results summarized in Table 4 show that Mandyphos and Taniaphos are versatile ligands with very good catalytic performances for a variety of substrate classes. For acrylic acid derivatives, itaconates and β-diketones, the performance was equal to or better than that known for leading commercial ligands. The basic profiling has shown that the choice of the substituents at the P atoms has a significant effect on the catalyst performance. Interestingly, for both ligand families, relatively electron rich aromatic substituents are most suitable for transformations with high enantioselectivity, whereas cyclohexyl (exception MAC) and CF_3-substituted aryl groups have a negative influence on ee and often the activity as well. This is in contrast to the Josiphos ligands with which several cases are known where these substituents are essential for good performance.[4]

4. Experimental

All ligands were prepared in analogy to the procedures published by Knochel and co-workers[5,6] and were fully characterized. All ligands can be obtained from Solvias and the derivatives listed in Table 5 are also available from Strem.

The hydrogenation experiments were carried out with the test substrates listed in Figures 4 and 8 in analogy as described in detail for two selected substrates below. The screening experiments were carried out in parallel in 10 mL glass vials. Selected single experiments were carried in larger glass vessels or stainless steel autoclaves.

Table 4. Comparison of the best ees of the Mandyphos and Taniaphos ligands with other ligand classes

Substrate class	Umicore ligand (not optimized)	Other commercial ferrocenyl ligands	Other commercial state of the art ligands
Disubstituted	**M4** (95%)	Josiphos (98%)	Rophos, Duphos Butiphane (99%)
α-Enamides	**T1** (>98%)		
Trisubstituted	**M4** (>98%)	Josiphos, Taniaphos[6] (99%)	Rophos, Duphos Butiphane (99%)
α-Enamides	**T1** (>96%)		
β-Enamides	**T1**, **T3** (up to 92%)	Josiphos (>95%)	Duphos, Bicp, Tangphos (99%)
Acrylic acids	**M4** (97%)	Walphos (>92%)	MeObiphep (>90%)
		Josiphos (98%)	
Itaconates	**T3** (>99%)	Josiphos (99%)	Butiphane, Duphos, FerroTANE (>95%)
		Rophos (>95%)	
α-Keto esters	**M4** (88%) **M1** (95%)[9]	Josiphos (60%)	MeObiphep (94%)
β-Keto esters	**T1** (95%)	Taniaphos (99%), Walphos (96%)	Binap, MeObiphep, Segphos (>99%)
β-Diketones	**T1** (>99%)	Walphos (96%)	Binap, MeObiphep, Segphos (>99%)

Table 5. Mandyphos and Taniaphos ligands available from Strem

Abbreviation	Solvias no Strem no CAS Reg. no	Name of ligand Acronym Molecular formula, MW	$[\alpha]_D^{20}$ Chemical purity Enantiomeric excess
M1	SL-M001-1	(αR,αR)-2,2′-Bis(α-*N*,*N*-dimethylaminophenylmethyl)-(*S*,*S*)-1,1′-bis(diphenylphosphino)ferrocene	>−320
	26-0252	(*R*)-(*S*)-NMe_2–PPh_2–Mandyphos	>97%
	[210842-74-3]	$C_{52}H_{50}FeN_2P_2$, 820.28	>99% ee
M2	SL-M002-1	(αR,αR)-2,2′-Bis(α-*N*,*N*-dimethylaminophenylmethyl)-(*S*,*S*)-1,1′-bis(dicyclohexylphosphino)ferrocene	>+54
	26-0240	(*R*)-(*S*)-NMe_2–PCy_2–Mandyphos	>97%
	[494227-35-9]	$C_{52}H_{74}FeN_2P_2$, 844.97	>99% ee
M3	SL-M003-1	(αR,αR)-2,2′-Bis(α-*N*,*N*-dimethylaminophenylmethyl)-(*S*,*S*)-1,1′-bis[di(bis-(3,5-trifluoromethyl)phenyl)phosphino]ferrocene	>−250
	26-0244	(*R*)-(*S*)-NMe_2–P(3,5-CF_3Ph)$_2$–Mandyphos	>97%
	[494227-36-0]	$C_{60}H_{42}F_{24}FeN_2P_2$, 1364.75	>99% ee
M4	SL-M004-1	(αR,αR)-2,2′-Bis(α-*N*,*N*-dimethylaminophenylmethyl)-(*S*,*S*)-1,1′-bis[di(3,5-dimethyl-4-methoxyphenyl)phosphino]ferrocene	>−61
	26-0248	(*R*)-(*S*)-NMe_2–P(3,5-Me-4–MeOPh)$_2$–Mandyphos	>97%
	[494227-37-1]	$C_{64}H_{74}FeN_2O_4P_2$, 1053.09	>99% ee
T1	SL-T001-1	(1*S*)-Diphenylphosphino-2-[(*R*)-α-(*N*,*N*-dimethylamino)-*o*-diphenylphosphinophenyl)methyl]ferrocene	>+312
	26-1155	(*R*)-(*S*)-Ph_2PPhCHNMe_2–T–PPh_2	>97%
	[255884-98-1]	$C_{43}H_{39}FeNP_2$, 687.56	>99% ee
T2	SL-T002-1	(*1S*)-Dicyclohexylphosphino-2-[(*R*)-α-(*N*,*N*-dimethylamino)-*o*-dicyclohexylphosphinophenyl)methyl]ferrocene	>+110
	26-0955	(*R*)-(*S*)-Cy_2PPhCHNMe_2–T–PCy_2	>97%
	[494227-38-2]	$C_{43}H_{63}FeNP_2$, 711.79	>99% ee

The reaction mixtures were analyzed by GC and HPLC methods using literature methods.

4.1. Ru catalyzed hydrogenation of acteylacetone (small scale single experiment)

The autoclave was purged with argon by setting the pressure to 40 bar and releasing it. This operation was repeated four times. The starting material acteylacetone (0.254 g, 2.53 mmol) and 5 mL of degassed methanol were placed in a 10 mL Schlenk flask with a stirring bar and a sequence high vacuum/argon-filing repeated six times. 60 μL of 1 M methanolic HCl was carefully added. In a 10 mL Schlenk flask (also under argon, same procedure as above) $[RuI_2(p\text{-cymene})]_2$ (6.2 mg; 0.0063 mmol) and **T1** (9.1 mg; 0.0133 mmol) were placed, and dissolved in methanol (5 mL). These solutions were stirred at room temperature for 10 min and then transferred via cannula to the autoclave with a gentle argon flow. The autoclave was purged with hydrogen (40 bar, four times), set at 60 bar. The autoclave was then heated up to 80 °C, and after 30 min, the hydrogen pressure set to 80 °C. After 16 h reaction time, the pressure was released. The clear reaction mixture was carefully evaporated to dryness under reduced pressure.

2,4-Pentanediol was quantitatively obtained (determined by GC and ^{1}H NMR). The predominant stereoisomer was (2*R*,4*R*)-pentanediol with a dl/meso ratio of 97.4:1.0 and an enantiomeric purity of 99.5% [determined after derivatization with trifluoroacetic anhydride using GC (column: Lipodex E, 50 m×0.25 mm, 80 °C, isothermic; carrier gas: H_2 120 kPa)].

4.2. Rh catalyzed hydrogenation of *Z*-acetamidocinnamate (scale up experiment)

The glass reactor was set under an atmosphere of argon by repeated sequences of high vacuum/argon-filling (four times). The starting material, methyl *Z*-acetamidocinnamate (13.18 g, 63.0 mmol), and 40 mL of degassed methanol were placed in a 100 mL Schlenk flask with a stirring bar and a sequence of high vacuum/argon-filling repeated six times. In a 100 mL Schlenk flask (also under argon, same procedure as above) $[Rh(nbd)_2]BF_4$ (1.2 mg; 0.0032 mmol) and **M4** (3.74 mg; 0.0036 mmol) were placed, and dissolved in methanol (40 mL). These solutions were stirred at room temperature for 10 min and then transferred via cannula to the glass reactor with a gentle argon flow. The reactor was purged with hydrogen/vacuum (1.2 bar/0.4 bar, six times), set at 1.05 bar hydrogen, the temperature maintained at 25 °C and stirring then started. After 7 h reaction time, the hydrogen was replaced by argon. The clear reaction mixture was evaporated to dryness under reduced pressure.

Conversion and enantiomeric purity were determined by using GC [Chirasil-L-Val: 30 m; 150 °C, 40, 10 min,

190 °C, 20 min; carrier gas: He (200 kPa)]. The conversion was quantitative and the enantiomeric excess of *N*-acetyl phenylalanine methyl ester determined to be 98.6% (*R*).

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