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Evaluation of Fe and Ru Pincer-Type Complexes as Catalysts for the Racemization of Secondary Benzylic Alcohols

Christoph Bornschein,+[a,b] Karl P. J. Gustafson,+[a] Oscar Verho,[a] Matthias Beller[b] and Jan-E. Bäckvall*[a]

Abstract: Herein, two Fe and Ru pincer-type catalysts are used for the racemization of benzylic alcohols. Racemization with the Fe catalyst was achieved within 30 minutes under mild reaction conditions, with a catalyst loading as low as 2 mol%. This reaction constitutes the first example of an iron-catalyzed racemization of an alcohol. The efficiency of the Fe catalyst and its Ru analogue was evaluated on a wide range of *sec*-benzylic alcohols. The commercially available Ru complex proved to be highly robust and even tolerated the presence of water in the reaction mixture.

The synthesis of enantiomerically pure compounds constitutes a fundamental part of modern organic chemistry. Asymmetric synthesis is widely applied in the preparation of pharmaceuticals,[1] electronic and optical devices,[2] polymer components[3] and biological probes.[4]

The resolution of racemates is still the most commonly used method for obtaining enantiomerically pure compounds on an industrial scale.[1c] A drawback of all resolution protocols is that only a maximum theoretical yield of 50% of the desired enantiomer can be obtained. To allow for quantitative yield, the undesired enantiomer has to be interconverted into the desired one e.g. via racemization. A coupling of resolution and racemization leads to a so-called dynamic kinetic resolution (DKR), where an *in situ* racemization catalyst keeps the starting material racemic.[5]

One of the most popular methods to racemize secondary alcohols involves reversible hydrogen transfer mediated by a metal catalyst that can be e.g. Ru-,[5a,6] Rh-[7] or Ir-[8] based.[9] [10] Racemization of alcohols can also be accomplished *via* a dehydration-hydration mechanism catalyzed by acidic zeolites[11] or resins.[12] There are also a number of substrate-specific catalysts, such as a vanadium catalyst that racemizes allylic alcohols[13] or a palladium catalyst that is mainly useful for allyllic esters.[14]

The development of metalloenzymnatic DKR began in the end of the 1990s[5a,15] and one of the racemizatiomn catalysts used was the Ru dimeric Shvo complex **1**.[16] Following this work, various Ru-cyclopentadienyl type transfer hydrogenation catalysts were developed that allow for an efficient racemization at ambient temperature.[17]

Recent efforts in optimizing such protocols have led to highly active and robust catalytic systems for the racemization of secondary alcohols in very short reaction times.[17] The Bäckvall group showed that racemization of secondary alcohols by pentaphenylcyclopentenylruthenium catalyst **2** (0.5 mol%) could be achieved in 10 minutes at ambient conditions,[6d,6e] which to date is one of the most versatile racemization catalysts for secondary alcohols. Later, Park and co-workers reported on a dimeric cyclopentenylruthenium complex **3** (2 mol%) that could be activated with light to obtain the desired racemization under mild conditions (30 °C, air) within 10 minutes reaction time.[18] A similar catalyst to **2** was created by the groups of Kanerva and Leino.[19] They developed the pentabenzyl analogue of **2**, a complementary catalyst working especially well on electron-rich alcohols, however, requiring slightly higher catalyst loadings. One example of a recently developed racemization catalyst is the Ru/indenyl complex **4** reported by the Nolan group.[6a, 20] By applying this complex to the racemization of (*S*)-1-phenylethanol, a complete racemization was achieved at room temperature (1 mol% catalyst) within 20 minutes. Furthermore, the group of Baratta has reported on a new type of racemization catalyst, composed of a pincer type Ru or Os catalyst working as racemization catalyst for secondary alcohols.[21]

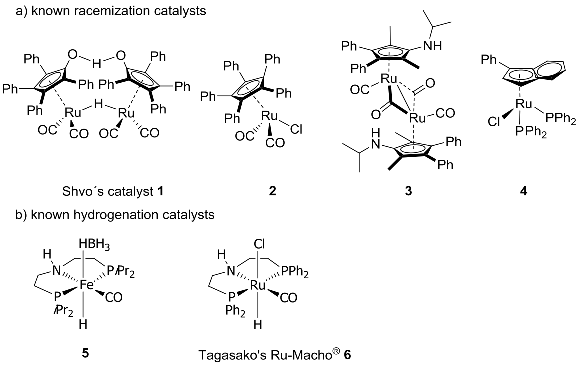

Figure 1. Powerful Ru-based racemization catalyst (a) and *PNP*-pincer-based de- and hydrogenation catalysts (b).

Despite the extensive research and the recent progress in the field of alcohol racemization, there is still a need of finding new and broadly applicable racemization catalysts that are cost-effective, easily accessible and composed of earth abundant elements. In line with these criteria, we decided to study the two *PNP*-pincer type catalysts **5** and **6**, which should be capable of mediating the racemization of alcohols given their dehydrogenation/hydrogenation properties. For instance, Ru-Macho® **6** is a commercially available and fairly inexpensive catalyst, which was previously used for the hydrogenation of ester derivatives.[22] The Fe-pincer catalyst **5** was recently utilized by the Beller group for the hydrogenation of carboxylic acid derivatives[23] and for the dehydrogenation of methanol.[24]

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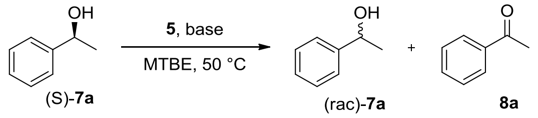

Table 1. Racemization of (*S*)-1-Phenylethanol (**7a**) using Fe-Pincer catalyst **5**.[a],[b]

Entry	Catalyst / mol%	Base / (mol%)	*ee*-value (rac)-**7a**[c]	Rel. amount of **8a**[c]
1	**2**	***t*-BuOK (4)**	**2%**	**5%**
2	1	*t*-BuOK (2)	82%	4%
3	0.5	*t*-BuOK (1)	99%	0%
4[d]	**2.5**	***t*-BuOK (5)**	**0%**	**5%**
5	2	*t*-BuOK (2)	99%	0%
6	2	*t*-BuOK (10)	7%	5%
7[e]	2	*t*-BuOK (4)	99%	0%
8	2	NaH (20)	99%	0%
9	2	NEt_3 (100)	84%	6%
10	2	Cs_2CO_3 (100)	99%	0%
11	2	Na_2CO_3 (100)	99%	0%
12	2	-	99%	0%

[a] General reaction conditions: 0.25 mmol (*S*)-**7a**, 1.25–6.25 µmol **5**, 0–0.25 mmol base, 1 mL MTBE, 50 °C, 30 min. [b] for complete optimization table see Supporting Information. [c] *ee*-values and yields of side product **8a** were determined by chiral GC. [d] 15 min reaction time. [e] 1 equiv. water was added to the reaction mixture.

The evaluation of catalysts **5** and **6** commenced with the racemization of 1-(*S*)-phenylethanol **7a**. First, the performance of the Fe-*PNP*-pincer complex **5** to racemize **7a** was evaluated in a set of different solvents, employing two equivalents of *t*-BuOK as base (Table S1, Supporting Information). Among the many solvents tested, only ethers (THF and MTBE) led to detectable racemization of **7a** (Table S1, entries 2, 3, 12 and 15-17). No racemization of **7a** was observed in other more strongly coordinating solvents, such as dimethyl formamide and 2-propanol[25] or in non-coordinating solvents, such as toluene, cyclohexane and pentane (Table S1, entries 18-22). MTBE was chosen as the solvent for further experiments with 2 mol% of **5** and 2 equivalents of *t*-BuOK (4 mol%) (Table 1, entry 1). These conditions allowed for a low amount of the undesired dehydrogenation product **8a** within the observed reaction time. The optimization showed that the amount of catalyst required is at least 2 mol% while with 1 and 0.5 mol% of **5** inefficient or no racemization was observed (entries 2 and 3). A slightly higher catalyst loading (2.5 mol%) led to a faster reaction and the reaction now gave full racemization within 15 min (Table 1, entry 4). The addition of 1 equiv. of water completely shut down the racemization (entry 5).

Next, the effect of different bases was studied and it was found that only *t*-BuOK promoted the desired racemization (Table 1, entries 1, 4 and vs. 6 and 8-11). In the absence of base in MTBE no racemization took place (entry 12).[26]

The influence of the relative amount of base, using 2 mol% of catalyst, that was required for sufficient activation was also studied (Table 1, entries 1, 5, 6 and 12). Two equivalents of base proved to be the most successful combination for achieving an efficient racemization (Table 1, entries 1 and 4).

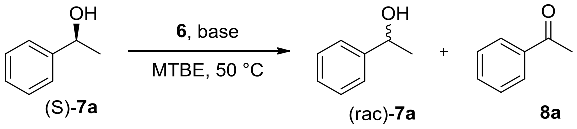

Table 2. Racemization of (*S*)-1-Phenylethanol (**7a**) using Ru-Macho® catalyst **6**.[a],[b]

Entry	Catalyst / mol%	Base / (mol%)	*ee*-value (rac)-7a[c]	Rel. amount of **8a**[c]
1	1	-	99%	0%
2	1	*t*-BuOK (2)	0%	2%
3	0.5	NaH (5)	5%	2%
4	0.5	Na_2CO_3 (100)	99%	0%
5[d]	**0.25**	***t*-BuOK (0.5)**	**0%**	**4%**
6 [e]	**0.5**	***t*-BuOK (1)**	**0%**	**3%**
7	0.5	*t*-BuOK (0.5)	7%	3%
8[f]	0.5	*t*-BuOK (1)	2%	2%
9[g]	0.5	*t*-BuOK (1)	0%	5%
10	0.1	*t*-BuOK (0.2)	99%	0%

[a] General reaction conditions: 0.5 mmol (*S*)-**7a**, 0.5–5.0 µmol **6**, 0–0.5 mmol base, 2 mL MTBE, 50 °C, 30 min. [b] for complete optimization table see Supporting Information. [c] *ee*-values and yields of side product **8a** were determined by chiral GC [d] 3 h reaction time [e] 10 min reaction time. [f]. 1 equiv. water was added to the reaction mixture. [g] reaction under air

In contrast to iron catalyst **5** the ruthenium catalyst **6** was found to exhibit a broader tolerance to the reaction conditions as complete racemization was observed in several solvents, such as toluene, THF and MTBE (Table S2), with either *t*-BuOK or NaH as bases (Table 2, entries 2 and 3). Even significant racemization was observed in 2-propanol as solvent (Table S2, entry 18). Gratifyingly, a catalyst loading as low as 0.25 mol% was sufficient for the racemization of **7a** within 3 h at 50 °C (Table 2, entry 5). By increasing the catalyst loading to 0.5 mol%, complete racemization was obtained within 10-15 min (Table 2, entry 6). An excess of base was required for maintaining high racemization activity, and consequently a 1:1 ratio between catalyst and base was insufficient for obtaining full racemization with in 30 min (Table 2, entry 7). Interestingly, further trials with addition of one equivalent of water, or even performing the reaction under air did not inhibit the activity of this catalyst (Table 2, entries 8 and 9). Additionally, the long-term stability was established by adding a second portion of the starting material after 1 h, showing a complete racemization after an additional hour.

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To establish the scope of Fe-complex **5**, it was evaluated for the racemization of a range of secondary alcohols (Figure 2). Various 1-phenylethanol derivatives with different substituents underwent efficient racemization with catalyst **5**. With *p*-methoxy and *p*-trifluoromethyl substituted aryls (**7b** and **7f)** a hydrogen atmosphere had to be applied to obtain full racemization. The 4-Br derivative **7c**, required four times longer reaction time compared to the other benzylic alcohols. Notably, the allylic alcohol **7j** was obtained fully racemic together with 21% of the unsaturated ketone. However, none of the usually observed isomerization side product was formed when **5** was used as catalyst. Furthermore, water- and oxygen-free reaction conditions were required for a satisfactory activity.

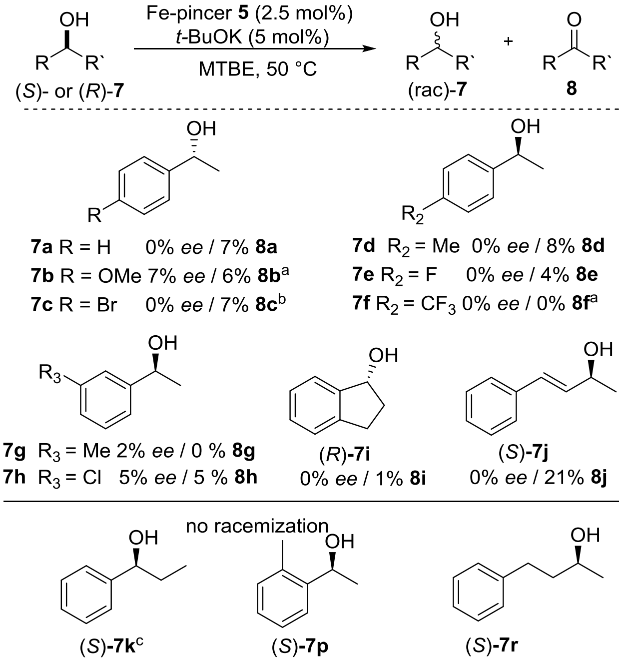

Figure 2. Substrate scope for the racemization of secondary alcohols. Reaction conditions (unless otherwise noted): secondary alcohol **7** (0.25 mmol), Fe-pincer (0.00625 mmol), *t*-BuOK (0.0125 mmol), *tert*-butyl methyl ether (MTBE, 1 mL), 50 °C, 30 min; enantiomeric excess (*ee*) was determined either with chiral GC/MS or HPLC. [a] 1 atm H_2-atmosphere during reaction; [b] 120 min reaction time. [c] (*S*)-**7m** 90% *ee*;.

The developed protocol for the Fe-catalyzed racemization was found to be sensitive to steric effects and substrates bearing a larger α-alkyl substituent (**7k**) or *ortho*-substitution (**7p**) were not tolerated. Also, the Fe-catalyst did not racemize aliphatic alcohols as demonstrated by the failed racemization of substrate **7r**.

Next, the optimized reaction conditions for the commercially available Ru-Macho® complex **6** were applied for the racemization of a variety of secondary alcohols (Figure 3). Interestingly, the Ru catalyst **6** displayed a broader substrate scope compared to its Fe analogue. It was found that an increased steric demand at the α-position had no noticeable influence on the performance of catalyst **6** (**7k**, **7l** and **7m**). Also, as in the case of the Fe catalyst **5**, no general trend in reactivity was observed for electron-withdrawing or -donating aryl substituents. Again, bromo-substituted substrates constitute an exception and needed prolonged reaction times. Nonetheless, 12 different *ortho*-, *meta*- and *para*-substituted 1-arylethanol derivatives worked excellently under the applied conditions. In the case of the 1-(*para*-cyanophenyl)ethanol (**7o**) an undesired catalyst-substrate interaction mediated by the nitrile group might be responsible for the incomplete racemization. It is worthy to note, that reducible nitrile- and nitro-functionalities stay intact throughout the experiments (GC/MS). Unfortunately, as for the Fe-analogue, the Ru-complex did not exhibit any racemization activity towards aliphatic alcohols.

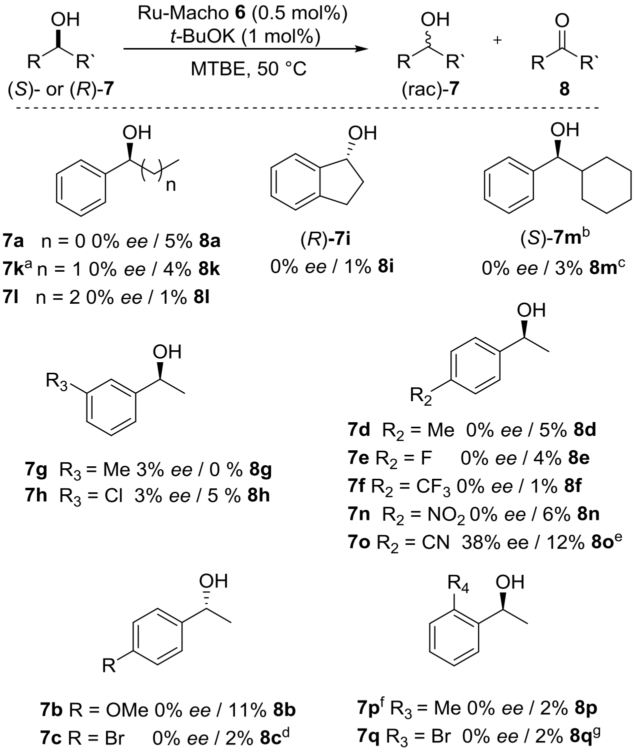

Figure 3. Substrate scope for the racemization of secondary alcohols. Reaction conditions (unless otherwise noted):: secondary alcohol **7** (0.5 mmol), Ru-Macho (0.0025 mmol), *t*-BuOK (0.005 mmol), MTBE (2 mL), 50 °C, 15 min. *ee*-value was determined either with chiral GC/MS or HPLC. [a] (*S*)-**7k** 90% *ee*; [b] (*S*)-**7m** 60% *ee*; [c] 30 min reaction time; [d] 120 min reaction time. [e] reaction in THF for 18h [f] (*S*)-**7t** 65% *ee.* [g] 60 min reaction time.

By comparing the performance of the two pincer catalysts, it was found that the Ru-Macho® catalyst is more stable and generally give lower amounts of the undesired ketone **8** than its Fe analogue. Attempts to use the racemization catalysts in a DKR were unsuccessful. When these catalysts were incorporated into a DKR protocol, no racemization was observed after the addition of various acyl donors. A strong interaction of the acyl donor with the active catalyst intermediate is likely to be responsible for this deactivation.

In conclusion, we have investigated the utility of two new pincer-type catalysts in the racemization of secondary alcohols. These two catalysts showed great activity in the racemization of benzyl alcohols. For the first time an iron-based catalyst was demonstrated to efficiently racemize alcohols. With this protocol

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racemization proceeds under mild reaction conditions, and within 30 minutes at 50 ^{o}C complete racemization had occurred. After activation by base, iron complex **5** racemized a range of 1-arylethanol derivatives as well as the allylic alcohol **7j**. Its Ru analogue proved to be more efficient, allowing for a broader substrate scope with lower catalyst loading, as well as tolerating the presence of water and air in the reaction mixture. Moreover, the Ru catalyst proved to be chemoselective and tolerated reducible groups such as nitro and nitrile groups, and in addition it worked well for sterically hindered substrates. These findings open up new possibilities for the development of racemization catalysts based on earth abundant transition metals. Future work will be dedicated to developing new Fe-based racemization catalysts that can be used in a chemoenzymatic DKR.

Experimental Section

Typical procedure for the Fe-catalyzed racemization of secondary alcohols. Fe-pincer catalyst **5** (2.5 mg, 0.00625 mmol) was dissolved in dry and degassed MTBE 1 mL. After achieving the desired reaction temperature of 50 °C, *t*-BuOK (1.4 mg, 0.0125 mmol) was added to the yellow solution, which caused an immediate color change to deep red. Shortly after base addition, the secondary alcohol **7** (0.25 mmol) was added to the reaction mixture under an argon atmosphere. After 30 minutes reaction time, an aliquot was withdrawn and analyzed by HPLC and/or GC.

Typical procedure for the Ru-catalyzed racemization of secondary alcohols Ru-Macho®-catalyst **6** (1.5 mg, 0.0025 mmol) was dissolved in dry and degassed MTBE 2 mL. After achieving the desired reaction temperature of 50 °C under argon, *t*-BuOK (0.6 mg, 0.005 mmol) was added to the reaction mixture, followed by the addition of secondary alcohol **7** (0.5 mmol). After 15 minutes reaction time an aliquot was withdrawn and analyzed by HPLC and/or GC.

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Keywords: iron • ruthenium • racemization • secondary alcohols • pincer-type catalysis

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[25] A possible reason why the iron catalyst did not work in 2-propanol could be due to strong interactions with the ligand back-bone. Since the concentration of the solvent is so high it outcompetes the starting material; see: S. Charkraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones, S. Schneider, ACS Catal. 2014, 4, 3994-4003.

[26] Noteworthy, in THF in the absence of base a complete loss of optical purity was achieved, however, significant amounts of dehydrogenation product, acetophenone **8a**, were formed (Table S1, entry 17).

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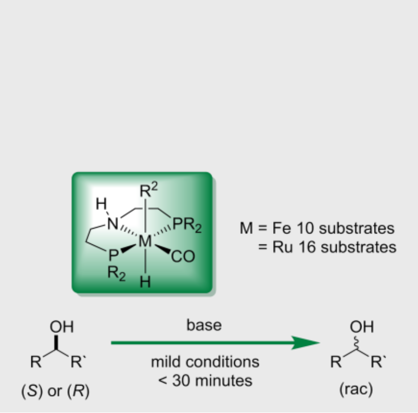
An efficient procedure for the racemization of secondary benzylic alcohols is presented. Using pincer-type complexes, the first Fe-catalyzed protocol was developed. The efficiency of the Fe catalyst and its Ru analogue was evaluated for a wide range of *sec*-benzylic alcohols. It was found that the commercially available Ru complex tolerates water and air in the reaction mixture during racemization.



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