

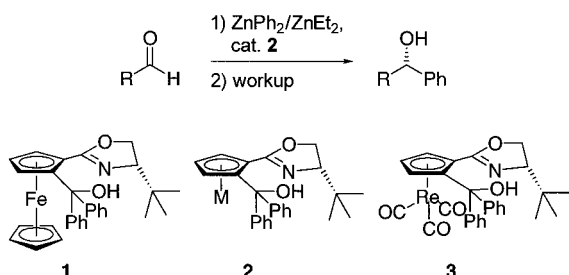
Application of a Planar Chiral η^5 -Cyclopentadienylrhodium(I)tricarbonyl Complex in Asymmetric Catalysis: Highly Enantioselective Phenyl Transfer to Aldehydes**

Carsten Bolm,* Martin Kesselgruber, Nina Hermanns, Jens P. Hildebrand, and Gerhard Raabe

Dedicated to Professor Günter Helmchen on the occasion of his 60th birthday

Asymmetric metal catalysis is one of the most active areas in modern organic chemistry, and the number of novel ligands for catalytic asymmetric transformations is growing rapidly.^[1] Among these compounds, planar chiral ferrocenes^[2] are of immense importance and some of them have already found application in industrial processes.^[3] Often, ferrocenes are superior to other metal π complexes,^[4] although for some catalyses it was found that a variation of the π -bound metal fragment can be of benefit.^[5]

Recently, we developed a system for the enantioselective, catalytic synthesis of diarylmethanol compounds from aldehydes by utilizing ferrocene **1**^[6] and a zinc species generated in situ from $\text{ZnPh}_2/\text{ZnEt}_2$ (Scheme 1).^[7] Further optimization of the process was expected to be possible by variation of the metal- π -fragment of **2**.^[8, 9] Herein, we describe the synthesis



Scheme 1. Enantioselective phenyl transfer onto aldehydes and catalytically active metal complexes.

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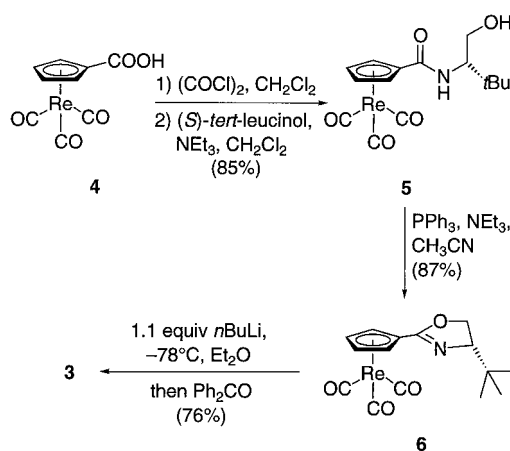
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Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

and application of novel cyrhetrene **3**, which was found to be superior in terms of both enantioselectivity and catalyst loading in the phenyl transfer to a wide variety of aldehydes.^[10]

Modifications of the metal- π -fragment of **2** were expected to have an impact on the steric and electronic properties of the catalyst. Assuming that decreased electron density on the ligand would result in increased Lewis acidity of the catalyst, we focussed our attention primarily on the synthesis of metal tricarbonyl complexes.^[9] There, the electron-withdrawing properties of the carbonyl groups would lower the electron density on the metal center as well as on the remaining cyclopentadienyl fragment bearing the stereogenic elements. If these electronic changes are then efficiently transferred to the catalytically active site and if the simultaneously occurring steric modifications are not counterproductive, beneficial effects in the catalysis could result. Due to its expected chemical stability rhodium(I) complex **3** appeared to be the complex of choice. To the best of our knowledge, η^5 -cyclopentadienylrhodium(I)tricarbonyl complexes have not been utilized in asymmetric catalysis, and only one nonracemic planar chiral derivative has been described.^[11, 12] Our synthesis of **3** started from cyrhetrenyl carboxylic acid **4**, which was obtained in a straightforward manner from $[\text{Re}_2(\text{CO})_{10}]$ and cyclopentadienyl carboxylic acid following an excellent, high-yielding procedure published by Jaouen et al.^[13] The cyrhetrenyl oxazoline **6**^[14] was synthesized in an analogous manner to the corresponding ferrocene derivatives via amide **5**, which was cyclized using the Appel protocol (Scheme 2).^[15] Directed



Scheme 2. Synthesis of complex **3**.

ortho-metalation^[16] of **6** using *n*BuLi in diethyl ether^[17] and subsequent quenching of the resulting lithiated species with benzophenone led to diastereomeric products in a ratio of 9:1 in favor of the product with *S,R*_p configuration.^[18] All transformations give good to excellent yields, and the compounds are crystalline and stable to air, light, and moisture.^[14]

To confirm the relative configuration of **3**, the solid-state structure of the cyrhetrenyl complex was determined by single-crystal X-ray structure analysis.^[14, 19] As depicted in Figure 1 one phenyl group of **1** is equatorial, while the other occupies an axial position with regard to the cyclopentadienyl

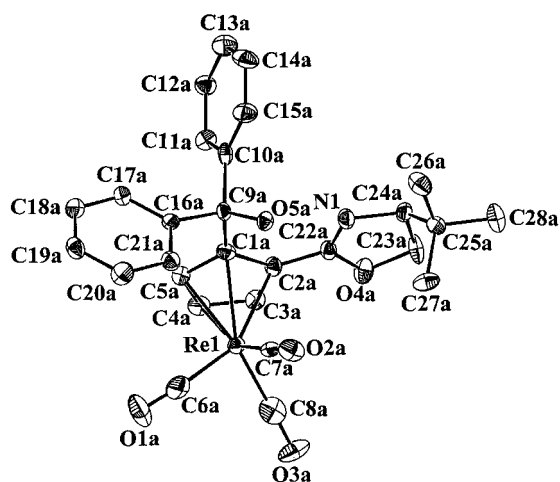


Figure 1. Structure of **3** (ORTEP plot; ellipsoids plotted with 50 % probability).

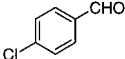
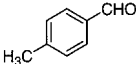
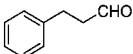
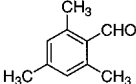
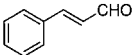
backbone. The relative location of the *tert*-butyl group at the oxazoline group is *trans* with respect to the axial phenyl group. Overall, the structural features of cyrhetrene **3** are very similar to those of ferrocene **1**, which suggested its potential use in catalysis.

The catalytic properties of **3** were explored in the asymmetric phenyl transfer from organozinc compounds to aldehydes. Initial approaches by ourselves^[7a] and others^[10] using diphenylzinc as phenyl source, encountered the difficulty that the uncatalyzed background reaction with the substrate is comparatively rapid, leading to a diminished enantioselectivity.^[20] The use of diethylzinc as an additive had been shown to be the key to significantly raise the enantiomeric excesses.^[7b, 10b] The replacement of the CpFe moiety by the Re(CO)₃ fragment now led to a further improvement of this transformation (Table 1).

For most examples, complex **3** shows higher enantioselectivity than ferrocene **1**. A significant increase was observed in reactions with *ortho*-substituted aldehydes (Table 1, entries 2 and 7) which are now among the best substrates for this transformation. Especially noteworthy is the result obtained with 2,4,6-trimethylbenzaldehyde (Table 1, entry 7; 98 % *ee*), which demonstrates that even *ortho*-disubstitution at the aromatic aldehyde is well tolerated. The reactions with other substrates follow trends that have previously been observed in catalyses with **1**: cinnamyl aldehyde displays lower levels of enantioselection (Table 1, entry 8), and aliphatic aldehydes are still somewhat problematic with respect to asymmetric induction (Table 1, entries 5 and 6). In several cases, even a catalyst loading of only 2 mol % of **3** was sufficient to achieve high *ee* values similar to the ones obtained with 10 mol % of **1** (Table 1, entries 1, 3, 5, 8).^[21]

In summary, we have described the synthesis of the η^5 -cyclopentadienylrhenium(i)tricarbonyl complex **3** and demonstrated its use in asymmetric catalysis. Compared to its analogous ferrocene derivative, cyrhetrene **3** shows significantly higher enantioselectivities in the catalyzed phenyl transfer from a phenylzinc species to aromatic and aliphatic aldehydes, leading to the currently most efficient approach for this reaction. Further studies are directed towards the use of

Table 1. Asymmetric phenyl transfer to various aldehydes.

$\text{R}-\text{CHO} \xrightarrow[\text{2) workup}]{\begin{array}{l} \text{1) ZnPh}_2 \text{ (0.65 equiv),} \\ \text{ZnEt}_2 \text{ (1.3 equiv),} \\ \text{cat. } \mathbf{3}, \text{ toluene, } 10^\circ\text{C} \end{array}} \text{R}-\text{CH}(\text{OH})-\text{Ph}$				
Entry ^[a]	Substrate	<i>ee</i> of product [%] ^[b,c] 2 mol % of 3	<i>ee</i> of product [%] ^[b,c] 10 mol % of 3	Absolute config. of alcohol ^[d]
1		96	98 (97)	<i>R</i>
2		83	96 (91)	<i>R</i>
3		95	95 (95)	<i>R</i>
4		85	99 (98)	<i>R</i>
5		76	83 (75)	<i>S</i>
6		74	78 (78)	<i>S</i>
7		80	98 (92)	<i>R</i>
8		88	92 (90)	<i>R</i>
9		93	98 (96)	<i>R</i>

[a] All reactions gave good to quantitative yields (>80 % on a 0.25 mmol scale). [b] Determined by HPLC using a chiral stationary phase. For exact separation conditions see Supporting Information. [c] Values in parentheses represent *ee* values obtained with 10 mol % of ferrocene ligand **1**. [d] Determined by comparison of the order of peak elution during HPLC with literature values, or tentatively assigned by assumption of an identical reaction pathway (entries 4, 6, 7, 9).

other η^5 -cyclopentadienylrhenium(i)tricarbonyl complexes in asymmetric catalysis.

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- [21] In a separate study (ref. [6c]), we had shown that the use of diastereomeric mixtures of **1** can lead to high enantioselectivity. As a consequence we proposed that this phenomenon could be exploited in cases where the directed *ortho*-metalation was not completely diastereoselective. Here we have now found that using 10 mol% of a 7:1 mixture of (*S,R*_p)-**3** and diastereomeric (*S,S*_p)-**3**, the phenylation of *p*-chlorobenzaldehyde proceeded with 97% *ee*. Thus, it appears that this mixture as such can be used in catalysis. The overall process applying **3** in the aryl transfer is thereby simplified even further.

Individual Alumina Nanotubes**

Lin Pu,* Ximao Bao, Jianping Zou, and Duan Feng

Avid attention has been given to the preparation, properties, and applications of nanotubes of different materials. Nanotubes composed of carbon,^[1] tungsten disulfide (WS₂),^[2] boron nitride (BN),^[3] vanadium oxide [VO_{2.40}(C₁₆H₃₃NH₂)],^[4] titanium dioxide (TiO₂),^[5] and others, were studied during the last decade. However, the reproducible usage of nanotubes in electrical devices is complicated by the fact that the tubes exist in different chiralities and diameters.^[6] Moreover, the raw materials consist of dense networks of closely connected nanotubes, and individual tubes are often obtained by ultrasonic agitation, which may introduce defects into the tubes.^[7] Here we report on two easy and controlled electrochemical-anodizing routes for the synthesis of individual alumina nanotubes (ANTs) in a single fabricating step. The structure of ANTs provides clues to unraveling the mechanism of nanotube growth and gives valuable hints on solving the long-standing problem of the self-organization mechanism in the porous anodization of aluminum.^[8–15]

Two different preparation methods (Figure 1), designated normal stepwise anodization (NSA) and lateral stepwise anodization (LSA), were used to make ANTs. The major difference between these two arrangements is the position on the sample (Al/Si) to which the potential difference *U* is applied. For NSA, it is the bottom surface of the Si substrate, and for LSA, the top surface of the Al metal film. This results in completely different current paths for the two methods. Note, however, that the orientation of the sample is not important.

The transmission electron microscope (TEM) images in Figure 2 show a general view of the ANTs. They are attached to the anodic porous alumina (APA) mother film. In the TEM

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