Hierarchically assembled helicates as reaction platform – from stoichiometric Diels–Alder reactions to enamine catalysis

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Abstract
The stereoselectivity of a Diels–Alder reaction within the periphery of hierarchically assembled titanium(IV) helicates formed from mixtures of achiral, reactive and chiral, unreactive ligands was investigated in detail. Following the pathway of the chiral induction, the chiral ligands, solvents as well as substituents at the dienophile were carefully varied. Based on the results of the stoichiometric reaction, a secondary amine-catalyzed nitro-Michael reaction is performed as well which afforded reasonable diastereoselectivities.

Introduction
Carbon–carbon (C–C) bond-forming reactions play a key role in organic chemistry. Hereby the stereoselectivity of the reaction is highly important due to the different behavior of stereoisomers in human metabolism [1,2]. Stereocontrol was achieved either via an auxiliary [3-7] or a catalyst [8], both providing the stereoinformation necessary for induction during the C–C bond formation. Catalytic approaches for C–C bond-forming reactions even found their way into the relatively young field of supramolecular chemistry, e.g., regioselective Diels–Alder reactions within supramolecular hosts as described by Fujita et al. [9-11] or stereoselective nucleophilic substitutions by Raymond et al. [12] are important examples in this context. Recently, we described the use of hierarchically assembled helicates as templates for stereoselective Diels–Alder reactions via a post-functionalization process [13]. Catechol ligands $\text{L-H}_2$ with an ester functionality in the 3-position were prepared via conversion of the acid chloride of 2,3-dihydroxybenzoic acid to the corresponding esters. These ligands underwent a complexation with titanoyl(IV) bisacetylacetonate and lithium carbonate initially forming a mononuclear “Werner-type” triscatecholate titanium(IV) complex. Two of these monomers dimerized in a consecutive step to obtain a non-covalently linked helicate
Scheme 1: Formation of hierarchically assembled lithium-bridged titanium(IV) helicates as well as the ligands used for the stereoselective Diels–Alder reaction.

Enantioselectivities up to 25% ee at elevated temperature (32% ee at 0 °C) depending on the substrate were achieved in a Diels–Alder reaction by introducing two different substituted catechol ester ligands during the complex formation: (1) A diene-substituted ligand 1-H$_2$ for the Diels–Alder reaction [21,22] and (2) a chiral ligand 2-H$_2$ for the stereocontrol [13].

Cleaving the complex under acidic conditions resulted in the desired enantiomerically enriched product 9 and enabled the recovery of the chiral ligand 2-H$_2$ (Scheme 2) [13].

The solvent choice allowed on/off-switching of the stereoselectivity of the Diels–Alder reaction. In THF the stereochemically locked dimer of the hierarchical helicate was present. Here stereoselectivity was turned on. On the other hand, the highly dynamic and fast diastereomerizing/epimerizing monomer was the major species in DMF switching off the stereoselectivity [13].

Herein we investigated the induction pathway and significantly optimized the stereoselectivity of the reaction. Furthermore, a catalytic approach was introduced which paves the way to the final goal of supramolecular stereoselective catalysis with hierarchical helicates as homogeneous catalysts.

Results and Discussion

Stereoselective Diels–Alder reactions in the periphery of hierarchically assembled helicates

Elucidating the induction pathway of the Diels–Alder reaction is vital for the optimization of the system described above and for the development of future processes based on the principle...
Scheme 2: Previously reported on/off switch for “remote-controlled” stereoselectivity of a Diels–Alder reaction by use of different solvents. The heteroleptic complexes are mixtures with an average ligand distribution as shown [13].

to use self-assembled coordination platforms (or as in the present case mixtures thereof) to control stereoselective C–C bond-forming reactions. Stereoinduction usually relies on spatial proximity of the prochiral carbon atoms and a chiral information of, e.g., a chiral auxiliary, Lewis acid or catalyst. In the previously reported system two different induction pathways were conceivable: (1) A chiral ligand is located close to the diene and controls the stereochemistry of the cycloaddition. (2) The chiral ligand controls the helicity of the helicate (ΔΔ or ΛΛ) and the helix induces the stereoselectivity of the Diels–Alder reaction.

To find out which of the induction pathways takes over the control of the Diels–Alder reaction in the periphery of the helicates, a specific helicity was induced at an achiral diene bearing helicate. It has been described before that an addition of chiral ammonium salts leads to the preference of a specific twist at the helicate [32]. As inductor, (R)-1-phenylethylammonium chloride was added to the racemic hexadiene-substituted helicate [Li3(1)6Ti2]−. The chiral salt influences the helicity of the monomeric complexes and which dimerize to the right-handed (ΔΔ) helicate [32]. As the process is slow, the mixture of the ammonium salt and complex was stirred for two weeks at room temperature in methanol. Thereafter, the solvent was removed and the Diels–Alder reaction with N-benzylmaleimide was performed at elevated temperature in THF. The reaction yielded the racemic product after purification. Scheme 3 is showing that the induction of stereochemistry of the Diels–Alder reaction depends on the chirality at the chiral ligand and not at the helix. This allows improvement of the stereoselectivity by using more appropriate sterically hindered or rigid chiral ligands. In addi-

Scheme 3: Elucidating the pathway of the stereoinduction of the Diels–Alder reaction. Ten equivalents of chiral ammonium salt are added to the hierarchical helicate in methanol and stirred for two weeks. Afterwards methanol is removed and the residue is dissolved in THF to perform a Diels–Alder reaction at the side chain.
Solvent dependence

Initially the solvent dependence of the stereochemical induction of the Diels–Alder reaction by the phenylethyl-derived ligand 2 was studied using N-benzylmaleimide (8e) as diene (Table 1). The solvents dioxane (17% ee) and acetone (14% ee) showed a slight decrease of the enantioselectivity compared to THF (21% ee). The yields of the reactions were rather moderate. On the other hand, the use of acetonitrile had no significant influence on the yield compared to acetone while the enantioselectivity dramatically dropped to 8% ee. In this case the lower selectivity correlated with the increasing lithium solvating capability of the solvent resulting in a higher proportion of the monomer and thus in lower stereoselectivities. In contrast to this, less polar solvents such as dichloromethane and chloroform resulted in increasing stereoselectivities in the Diels–Alder reaction due to their poor ability to stabilize lithium cations. Chloroform showed the best induction with 32% ee followed by dichloromethane with 25% ee, both with 50% yield (Table 1).

Ligand screening

In a second optimization step, the chiral ligands have been varied. An increase of stereoselectivity was achieved by using the helicates with a statistical ligand distribution Li[Li3(1)(L*)3]2] (L* = 3–7-H2). The given formula only describes the ratio of the ligands but in fact a statistical mixture of complexes Li[Li3(L*)6Ti2], Li[Li3(1)(L*)5Ti2], Li[Li3(12)(L*)4Ti2], Li[Li3(13)(L*)3Ti2], Li[Li3(14)(L*)2Ti2], Li[Li3(15)(L*)1Ti2], and Li[Li3(16)2Ti2] is present. Expanding the aromatic unit to a naphthyl group in 3-H2 resulted in an increase of the enantioselectivity to 44% ee. Even better selectivities were obtained with 4-H2 bearing an indanyl [33,34] substituent which combines a stereogenic center implemented in a ring system providing rigidity as well as an aromatic residue. The enantioselectivity increased to 58% ee (Table 1).

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Table 1: Optimization of the stereoselectivity achieved of the Diels–Alder reaction at hierarchical helicates with solvent and chiral ligand screening.

| Entry | L* | 9 | R | solvent | T [°C] | yield [%] | ee [%] |
|-------|----|---|---|---------|--------|-----------|--------|
| 1     | 2  | e | Bz | THF     | 70     | 77 [13]   | 21 [13]|
| 2     | 2  | e | Bz | dioxane | 105    | 53        | 17     |
| 3     | 2  | e | Bz | acetone | 60     | 50        | 14     |
| 4     | 2  | e | Bz | MeCN    | 86     | 44        | 8      |
| 5     | 2  | e | Bz | DCM     | 44     | 50        | 25     |
| 6     | 2  | e | Bz | CHCl3   | 65     | 50        | 32     |
| 7     | 3  | e | Bz | CHCl3   | 65     | 71        | 44     |
| 8     | 4  | e | Bz | CHCl3   | 65     | 64        | 58     |
| 9     | 5  | e | Bz | CHCl3   | 65     | 61        | 46     |
| 10    | 6  | e | Bz | CHCl3   | 65     | 64        | 16     |
| 11    | 7  | e | Bz | CHCl3   | 65     | 11        | –8     |
| 12    | 4  | a | Me | CHCl3   | 65     | 76        | 43     |
| 13    | 4  | b | Et | CHCl3   | 65     | 79        | 39     |
| 14    | 4  | c | t-Bu | CHCl3 | 65     | 82        | 18     |
| 15    | 4  | d | Cy | CHCl3   | 65     | 80        | 49     |

*Reactions performed in closed tubes.
Besides the aromatic ligands, terpenyl-substituted ligands were investigated, too. The largest ligand $7\text{-H}_2$ with a cholesteryl moiety favored the opposite enantiomer, however, only with $\sim 8\%$ ee in only $11\%$ yield. The low yield may be attributed to the poor solubility of the helicate. The other terpene [35,36] derived systems $\text{Li[Li}_3(1\text{)}(3\text{)}\text{Ti}_2\text{]}$ and $\text{Li[Li}_3(1\text{)}(3\text{)}\text{Ti}_2\text{]}$ showed a different behavior. The (15,2S,35,5R)-3-pinanyl-substituted $\text{Li[Li}_3(1\text{)}(3\text{)}\text{Ti}_2\text{]}$ yielded $46\%$ ee, while the complex bearing a 1-(-)-borneyl residue $\text{Li[Li}_3(1\text{)}(3\text{)}\text{Ti}_2\text{]}$ showed only $16\%$ ee. The yields were higher than $60\%$. A possible reason for the significant drop in enantioselectivity by switching from ligand 5 to 6 was due to the different dimerization behavior. The homoleptic helicate $\text{Li[Li}_3(6\text{)}\text{Ti}_2\text{]}$ shows a lower dimerization tendency compared to $\text{Li[Li}_3(5\text{)}\text{Ti}_2\text{]}$ [35,36]. Thus, the higher amount of undesired monomer in solution of $\text{Li[Li}_3(1\text{)}(3\text{)}\text{Ti}_2\text{]}$ resulted in a partial switch-off of the stereoselectivity.

**Screening of the dienophile**

The variation of the dienophile was studied in chloroform using the helicate $\text{Li}_4(1\text{)}(4\text{)}\text{Ti}_2\text{]}$. $N$-Maleimides $8\text{a}$ and $8\text{b}$ with a methyl and an ethyl residue showed higher yields and a lower induction in comparison to the benzyl derivative $8\text{e}$ with $43\%$ ee and $39\%$ ee (Table 1). The poorest result was obtained by using dienophile $8\text{e}$ with a tert-butyl substituent ($82\%$ yield, $43\%$ ee and $80\%$ ee (Table 1). The poorest result was obtained by using dienophile $8\text{e}$ with a tert-butyl substituent ($82\%$ yield, $43\%$ ee and $80\%$ ee (Table 1). The obtained ligands $13\text{a-d-H}_2$ were used together with the chiral ligands $2,4,5\text{-H}_2$ for the formation of hierarchical helicates with a statistical ligand ratio which were formed from 1 equivalent of $13\text{-H}_2$ and 5 equivalents of $2\text{-H}_2$, $4\text{-H}_2$, and $5\text{-H}_2$.

The catalytic activity of the amine ligands was tested first by using the uncoordinated ligand $13\text{a-H}_2$ substituted with a N-methylethylamine moiety. The reaction was performed in DMSO-$d_6$ due to solubility limitations of the ligand. Fast and easy measurement of the yield and the diastereoselectivity was possible by NMR spectroscopy. The nitro-Michael reaction of 3 equivalents propenal ($14\text{)}$ and $6\text{-nitrostyrene}\text{(15)}$ with $25\%$ yield of product $16$ and a nearly 1:1 diastereomeric ratio (Table 2).
Enamine-catalyzed nitro-Michael reaction with hierarchically assembled helicates.

Catalysts at the “statistical” helicates was carried out with 5 equivalents of propanal (14) in order to gain a higher conversion. Beside a significant control over the diastereomeric ratio no enantioselectivity was achieved with helicates as catalysts. Catalysts at concentrations of 15 mol % were used in CDCl₃ at room temperature and 0 °C with three or seven days of reaction time. The conversion was controlled by NMR spectroscopy and TLC. The helicate Li₄[(13a)₁(2)ₛT₁₂] did not lead to any conversion at room temperature (Table 2). The catalyst Li₄[(13b)₁(2)ₛT₁₂] with an ethyl-substituted amine worked well resulting in 88% yield and 66% de at room temperature. The diastereomeric excess increased slightly to a maximum of 74% de (dr 87:13) at 0 °C. A dramatic decrease to 30% de was observed by lowering the catalyst loading to 7.5 mol % while increasing the temperature to 70 °C. No enantioselectivity was observed using the helicate Li₄[(13b)₁(2)ₛT₁₂] as catalyst. The helicates Li₄[(13c)₁(2)ₛT₁₂] and Li₄[(13d)₁(2)ₛT₁₂] with an isopropyl-substituted ethylamine and a cyclic secondary amine ligand as catalytically active unit showed no conversion in the nitro-Michael reaction. Solubility problems were the supposed reason for this observation. Thus, the amine ligand 13b-H₂ seemed to be an appropriate component to make helicates from ligand mixtures which possess catalytic activity.

Exchange of the chiral ligand 2 by other chiral ones resulted in the corresponding complexes Li₄[(13b)₁(4)₄T₁₂] and Li₄[(13b)₁(5)₅T₁₂], but did not lead to a control of enantioselectivity. A reasonable diastereoselectivity of 60% de was observed for both catalysts. The limited solubility of these complexes caused a significant reduction of the yield at room temperature and due to this the reaction was not performed at lower temperatures.

### Conclusion

An optimization of the Diels–Alder reaction taking place in the periphery of hierarchically assembled helicates was carried out. It was based on the elucidated induction pathway showing that the stereoselectivity was due to the proximity of the chiral units of ligand 2 to the diene unit. The helicity of the helicate did not have a significant influence. After optimization of solvent, chiral ligand, and substituent at the dienophile stereoselectivity was nearly tripled. Up to 58% ee was achieved in the Diels–Alder reaction in chloroform with the indanyl-substituted chiral ligand 4-H₂ and N-benzylmaleimide (8e) as the dienophile.

In addition, the transition from the stoichiometric Diels–Alder reaction to a catalytic nitro-Michael reaction was described utilizing secondary amine ligands as catalysts. Only amine ligand 13b-H₂ seemed suitable in the catalysis with the corresponding statistical helicates. With other complexes solubility problems arose. Li₄[(13b)₁(2)ₛT₁₂] was the most efficient catalyst discussed in this study and provided good yields of up to 88% at room temperature. Suitable diastereoselectivities were

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**Table 2: Enamine-catalyzed nitro-Michael reaction with hierarchically assembled helicates.**

| Entry | Catalyst | mol % | T [°C] | t [d] | Yield [%] | dr |
|-------|----------|-------|--------|------|-----------|----|
| 1ᵇ    | 13a-H₂   | 25    | rt     | 2    | 45⁰      | 52:48⁰ |
| 2     | Li₄[(13a)₁(2)ₛT₁₂] | 15   | rt     | 3    | 0        | –   |
| 3     | Li₄[(13b)₁(2)ₛT₁₂] | 15   | rt     | 3    | 88       | 83:17 |
| 4     | Li₄[(13b)₁(2)ₛT₁₂] | 15   | 0      | 7    | 71       | 87:13 |
| 5     | Li₄[(13b)₁(2)ₛT₁₂] | 7.5  | 70     | 1    | 48       | 65:35 |
| 6     | Li₄[(13c)₁(2)ₛT₁₂] | 15   | rt     | 3    | 0        | –   |
| 7     | Li₄[(13d)₁(2)ₛT₁₂] | 15   | rt     | 3    | 0        | –   |
| 8     | Li₄[(13b)₁(4)₄T₁₂] | 15   | rt     | 3    | 13       | 80:20 |
| 9     | Li₄[(13b)₁(5)₅T₁₂] | 15   | rt     | 3    | 27       | 80:20 |

ᵃNo enantioselective was achieved.ᵇReaction was performed in DMSO-d₆ (0.26 M) due to solubility limitations of the free ligand with 3 equiv of propanal. ⁰Values determined by integration of the crude NMR spectrum of the reaction.
obtained with up to 74% de (dr 87:13) at 0 °C and 66% de (dr 83:17) at room temperature. Enantioselectivity was not achieved even with the chiral ligands 4-H₂ and 5-H₂. Nevertheless, the successful implementation of diastereoselective catalysis by hierarchically assembled helicates was a big step forward and will draw our focus on the development of new systems possessing catalytic activity with improved solubility.

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