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Highly Enantioselective Allylation of Imines with a Chiral Zirconium Catalyst**

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Over the past several years, powerful asymmetric catalytic variants for many basic synthetic reactions have been developed,[1] and in this large and fast-expanding area of chemistry, several chiral Lewis acids have been successfully used as catalysts.[2] Although highly effective methods that follow this approach for the catalytic asymmetric alkylation of carbonyl compounds have been reported,[3] only very few examples are known for their aza analogues.[4] In the case of imines, the Lewis acids are often deactivated or decomposed by the nitrogen atoms of the starting materials or products, and therefore, catalytic reactions are difficult to perform.

The synthesis of chiral homoallylic amines is of particular interest since they can be used as versatile synthetic intermediates and can be easily converted into many different functional groups.[5] The first catalytic asymmetric allylation of imines was reported in 1998 by Yamamoto and co-workers using allyltributylstannane in the presence of a chiral π-allylpalladium complex.[6] In 1999, Jørgensen and co-workers reported the catalytic asymmetric allylation of α-imino esters.[7] In recent reports, we have demonstrated the extraordinary potential of zirconium(IV) as a metal center for the design of chiral Lewis acid catalysts that are suitable for the activation of bidentate imino compounds in an efficient way.[8]

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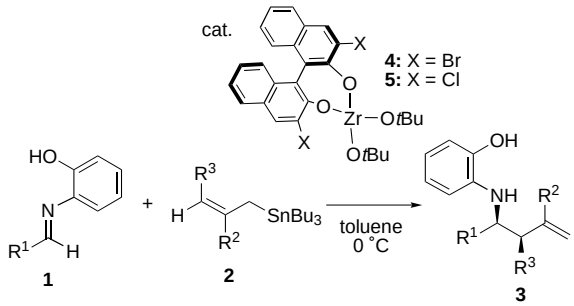
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

In this paper, the viability of this approach is illustrated by the allylation of imines **1** with allylstannanes **2** to afford the corresponding homoallylic amines **3** in good yields and with high stereoselectivities (Scheme 1).



1a: R^1 = Ph
1b: R^1 = 1-naphthyl
1c: R^1 = 3,4-$(OCH_2O)C_6H_3$
1d: R^1 = 2,3-$(MeO)_2C_6H_3$
1e: R^1 = 2-furyl
1f: R^1 = *p*-ClC_6H_4

2a: R^2 = CH_3, R^3 = H
2b: R^2 = CH_2OTBS, R^3 = H
2c: R^2 = CH_2OH, R^3 = H
2d: R^2 = CH_2OH, R^3 = CH_3

Scheme 1. Catalytic asymmetric allylation of imines. TBS = *tert*-butyldimethylsilyl.

We first screened different BINOL derivatives and additives, and found that preparation of the catalyst in situ from $Zr(OtBu)_4$ and an equimolar amount of (*R*)-3,3′-dibromo-1,1′-bi-2-naphthol ((*R*)-3,3′-Br_2BINOL) or (*R*)-3,3′-dichloro-1,1′-bi-2-naphthol ((*R*)-3,3′-Cl_2BINOL) in toluene gave the best results.[9] Conversion of imine **1a** was carried out with stannanes **2a – c** (Table 1). The use of **2a** and **2b** resulted in modest enantioselectivities,[10] and reaction times up to 30 hours were required. A remarkable acceleration of the reaction rate and improved enantioselectivities were observed with stannane **2c** in which the alcohol functionality is unprotected.[10] The reaction was completed within 2 hours, and an 86% yield and an enantiomeric excess of 83% were obtained. In an attempt to extend the scope of this reaction, allylstannane **2d**, with a methyl substituent at the C-3 position, has also been studied.[11] As can be seen from Table 2, improved enantioselectivities and excellent *syn*/*anti* ratios were obtained. The absolute configuration of **3cd** (R^1 = 3,4-$(OCH_2O)C_6H_3$, R^2 = CH_2OH, R^3 = CH_3) was determined to be 3*R*,4*S* by X-ray crystal structure analysis.[12] Interestingly, nearly identical yields and asymmetric inductions were observed with catalysts **4** and **5**. However, catalyst **5**

Table 1. Enantioselective allylation of imines with allylstannanes **2a – c**[a].

Entry	Imine	Stannane	Yield [%]	*ee* [%]
1	**1a**	**2a**	74	55
2	**1a**	**2b**	74	54
3	**1a**	**2c**	86	83
4	**1b**	**2c**	91	68

[a] 10 mol% of catalyst **4** was used.

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Table 2. Enantioselective allylation of imines with allylstannane **2d**.

Entry	Catalyst[a]	Imine	Yield [%][b]	*ee* [%]
1	**4**	**1a**	84	93
2	**4**	**1b**	81	95
3	**4**	**1c**	72	91
4	**4**	**1d**	71	94
5	**5**	**1e**	76	92
6	**4**	**1f**	78	87

[a] 10 mol % of catalyst was used. [b] The *syn*:*anti* ratio was determined by NMR spectroscopic analysis to be >95:5 in all cases.

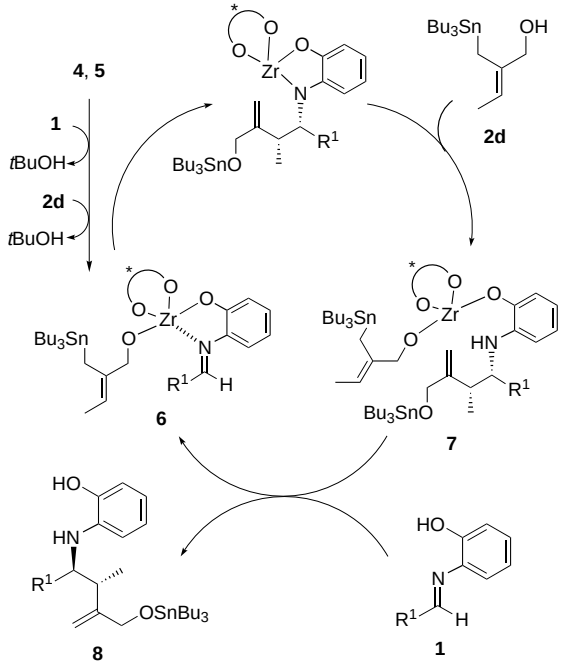
Table 3. Enantioselective allylation of imines with allylstannane **2c** with the use of a novel Zr catalyst prepared with methanol as an additive.

Entry	Catalyst[a]	Imine	Yield [%]	*ee* [%]
1	**4**	**1a**	77	96
2	**5**	**1b**	85	97
3	**4**	**1c**	84	99
4	**4**	**1d**	80	87
5	**4**	**1e**	68	96

[a] 10 mol % of catalyst was used.

showed a beneficial effect on the yield in the reaction of **1e** (Table 2, entry 5).[13]

The proposed catalytic cycle of this asymmetric reaction is shown in Scheme 2. The active catalyst is generated by the bonding of the alcohol functionalities of imine **1** and



Scheme 2. Proposed catalytic cycle. The asterisk represents the position of the BINOL derivative.

allylstannane **2d** to the zirconium center.[14] In an intramolecular reaction, the allylstannane attacks the carbon–nitrogen double bond in an ene-like fashion, which leads to intermediate **7**.[15] The product **8** is released from the zirconium center and the intermediate **6** is regenerated by bonding of **1** to the zirconium.

In addition, excellent results for the reaction of allylstannane **2c** were observed when the catalyst **4** or **5** was prepared in THF with addition of two equivalents of methanol as an additive (Table 3). After preparation of the catalyst, the THF was evaporated and the reaction was performed in toluene as described.[16] This modified catalyst system resulted in significantly improved enantioselectivities. While the 83 % *ee* value in the reaction of **1a** with **2c** was improved to 96 % *ee* (Table 1, entry 3, and Table 3, entry 1), the 67 % *ee* value in the reaction of **1b** with **2c** with catalyst **5** was further improved to 97 % *ee* when the new catalyst system was used. Furthermore, a 99 % *ee* for the *syn* adduct (*syn*/*anti* > 95:5) was obtained in the reaction of **1a** with **2d**. Although NMR studies gave almost no valuable information on the structure of the new catalyst, it was revealed from control experiments that the use of water instead of methanol was also effective, and that even one equivalent of the additive was sufficient to get comparable results. We assume at this stage that the effect of the additive is to deoligomerize the less selective oligomeric catalyst structures; this would result in the formation of the desired active monomeric catalyst species.[17]

In summary, we have developed a very efficient procedure to synthesize substituted homoallylic amines from imines in an asymmetric catalytic manner. High yields and high levels of diastereo- and enantioselectivity were obtained for all substrates. The expansion of this basic concept, which provides a convenient entry into various chiral building blocks, and further mechanistic studies to clarify the exact structure of the catalyst and the mechanism of the reaction are currently in progress.

Experimental Section

Representative experimental procedure for the reaction of imines **1** and allylstannanes **2**: (*R*)-3,3′-Br_2BINOL (0.13 mmol) was added to a solution of $Zr(OtBu)_4$ (0.13 mmol) in toluene (5.0 mL). The solution was stirred for 1 h at room temperature and then cooled to 0 °C. Compounds **1a** (1.3 mmol) and **2d** (1.3 mmol) were successively added in toluene (2.5 mL each). The mixture was stirred for 12 h, quenched with a saturated aqueous solution of $NaHCO_3$, and extracted with diethyl ether. After a standard workup, the crude product was purified by column chromatography on silica gel to give the desired adduct. The diastereomer ratio was determined by NMR spectroscopic analysis, and the optical purity was determined by HPLC analysis with a chiral column.[16]

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[12] The absolute configuration assignment was made by X-ray crystal structure analysis after converting **3cd** into its (1*S*)-camphanic diester. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157494. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] For the effect of the hydroxyamino moiety of imines and for deprotection of this moiety of the product to form the free amino group, see ref. [8a].

[14] In NMR spectroscopic experiments, we were able to show that an allyl alcohol, as a model compound, was bonded to the zirconium center of the catalyst. From this observation, it is assumed that bonding of allylstannnane **2c** to the zirconium leads to a better-organized transition state and, therefore, to higher enantioselectivities and even accelerated reaction rates. When equimolar amounts of **4** and **2d** were mixed and imine **1a** was then added after 1 h, no formation of the product was observed. An allyltransfer from tin to zirconium is likely to be the reason for this observation (A. L. Costa, M. G. Piazza, E. Tagliavini, C. Trombini, A. Umani-Ronchi, *J. Am. Chem. Soc.* **1993**, *115*, 7001 – 7002). Also from the product formed when **2d** is the substrate, we can rule out the idea that an allyltransfer from zirconium to imine is the actual reaction pathway.

[15] The relative and absolute configuration of the product would be explained by assuming this catalytic cycle.

[16] Details are shown in Supporting Information.

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Noncoordinating Dendrimer Polyanions: Cocatalysts for the Metallocene-Catalyzed Olefin Polymerization

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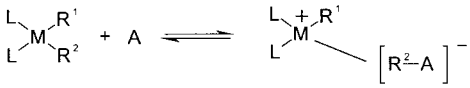
The metallocene-catalyzed polymerization of nonpolar monomers (in particular α olefins) allows the production of polymers with new architectures and properties.[1] In addition, because of their high activity, metallocene catalyst systems are used in very small amounts and can be left in the product, simplifying the polymer work up. During the polymerization the activated metallocene complex is present as a cation $[L_2MR^1]^+$ that is stabilized by an noncoordinating anion $[R^2A]^-$.[2, 3] This contact ion pair can be formed by treating a neutral metallocene with an activating cocatalyst that can abstract a ligand from the metallocene [Eq. (1)]. To date the



(1)

most important industrial examples of such cocatalysts have been methylaluminoxane (MAO),[4, 5] a condensation product prepared from $AlMe_3$ and water, which has a complex structure, and the perfluorphenylborane $B(C_6F_5)_3$.[3g, 6, 7] The interaction within the ion pair $[L_2MR^1]^+[R^2A]^-$ for a given ligand system L has an important influence on the catalytic properties such as activity, life time of the active species, chain-termination and chain-transfer reactions, and regio- and stereoregularity.[3w,x, 8] Thus there is increased interest in the synthesis of new, noncoordinating anions that are less nucleophilic; this can be achieved by the extensive delocalization of the negative charge[9] or steric shielding[3x, 10]. Tris(perfluorobiphenyl)alkylborates,[11] (perfluoroaryl)fluoroaluminates,[12] and triorganosilyl-substituted tetrakis(perfluorophenyl)borates[13] are examples of anions which, in addition to a delocalization of the charge, are sterically more demanding than $[R^2B(C_6F_5)_3]^-$. We wished to study the polymerization properties of metallocene – cation – anion pairs in which the anion is extremely sterically demanding; dendrimers, defined, highly branched, and highly functionalized, space-filling molecules have not been used in this context before.[14] Carbosilane dendrimers appeared to be particularly suitable in that the Si–C bond is basically chemically inert and thus side reactions (such as degradation of the dendrimer) during synthesis or the polymerization are unlikely.[15] The new polyanionic carbosilanes **IVa – c** are the first noncoordinating polyanions to be based on dendrimers. The construction of the Si–C framework was by means of alternating hydrosilation and Grignard reactions starting from tetravinylsilane, followed by hydroboration of the resulting allylsilyl dendrimer

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