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Catalytic asymmetric hydroamination of non-activated olefins

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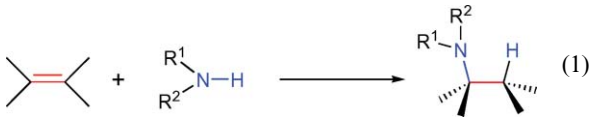
Hydroamination is a highly atom-economical process in which an amine N–H functionality is added to an unsaturated carbon–carbon linkage. This potentially highly useful process gives access to various nitrogen-containing basic and fine chemicals as well as naturally occurring alkaloid skeletons. Asymmetric hydroamination reactions promoted by chiral catalysts are particularly attractive. This review highlights recent progress in the development of early transition metal catalysts for the asymmetric hydroamination of non-activated alkenes.

Introduction

The efficient synthesis of nitrogen-containing compounds has sparked significant research efforts, due to their high relevance in biological systems and industrially important basic and fine chemicals. Although many synthetic methods have been devised over the last century,[1] one of the simplest synthetic approaches, the hydroamination, has become only the focus of attention with the advent of transition metal catalysts. The addition of amine N–H functionalities to unsaturated carbon–carbon bonds, either in an *inter*molecular [eqn. (1)] or *intra*molecular [eqn. (2)] fashion, generates amines in a waste-free, highly atom-economical manner starting from simple and inexpensive precursors.[2]



(1)

Kai Carsten Hultzsch studied chemistry at the University of Mainz and Toronto from 1991 to 1996. He finished his PhD in 1999 under the guidance of Jun Okuda in Mainz. After two years as a Feodor Lynen postdoctoral fellow in the group of Richard R. Schrock at MIT, he began his independent research career in 2001 as a DFG Emmy Noether fellow at the University of Erlangen-Nürnberg. He is the recipient of the Wöhler young investigator award and the ADUC award for habilitands. His main areas of interest are transition metal catalysed stereoselective olefin heterofunctionalisations, as well as (co)polymerisation of non-polar and polar monomers.

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(2)

Although the direct addition of amines to alkenes is thermodynamically feasible ($\Delta H^\circ \approx -52.7$ kJ mol^{-1}, $\Delta S^\circ \approx -127.3$ J K^{-1} mol^{-1} for the addition of ammonia to ethylene),[2a,b] the hydroamination usually requires assistance from a catalyst:

- an electrostatic repulsion between the nitrogen lone pair of the approaching amine and the π-bond of the electron-rich olefin results in a high activation barrier;
- a concerted [2 + 2] addition of the N–H bond to the alkene is an orbital-symmetry forbidden process and is unfavourable due to the large difference in energy between the carbon–carbon π-bond and the N–H σ-bond;
- the equilibrium is shifted towards the starting materials at elevated temperatures due to the negative reaction entropy.

Therefore, uncatalysed additions are commonly only observed in hydroamination reactions of activated, electron-deficient alkenes.[3] Increasing research effort has led to the development of many transition metal based catalyst systems (early transition metals of groups 3–5, lanthanides and actinides,[2g,h] and late transition metals of groups 8–10[2f]) over the last two decades. Despite this progress, substrate diversity for most catalyst systems has remained limited.

Because of the chirality of many hydroamination products, asymmetric hydroamination (AHA) carried out with chiral catalysts is an attractive, but highly challenging task.[4] This review will focus in particular on the progress in the catalytic asymmetric hydroamination of non-activated alkenes, a domain for rare earth metal complexes and more recently also group 4 metal catalysts. Asymmetric hydroamination of activated alkenes (vinyl arenes,[5a–c] 1,3-dienes,[5d] norbornene[5e]) or alkynes,[5f] a typical domain of late transition metal catalysts, is out of the scope of this review. Furthermore, asymmetric aza-Michael reactions,[6] in which the catalyst merely plays the role of a chiral Lewis acid, will not be covered.

Rare earth metal based catalysts

The synthesis and handling of organometallic compounds of the rare earth metals (including Sc, Y, La to Lu) is complicated by their high sensitivity towards air and moisture. Nevertheless, their unique chemical behaviour and high activity in a wide variety of catalytic applications[7] has fuelled intensive research efforts. With improved and simplified synthetic protocols, *e.g.* alkane or amine elimination routes, these catalysts can often be prepared *in situ* using standard Schlenk line and glove box techniques. However, major drawbacks remain, such as

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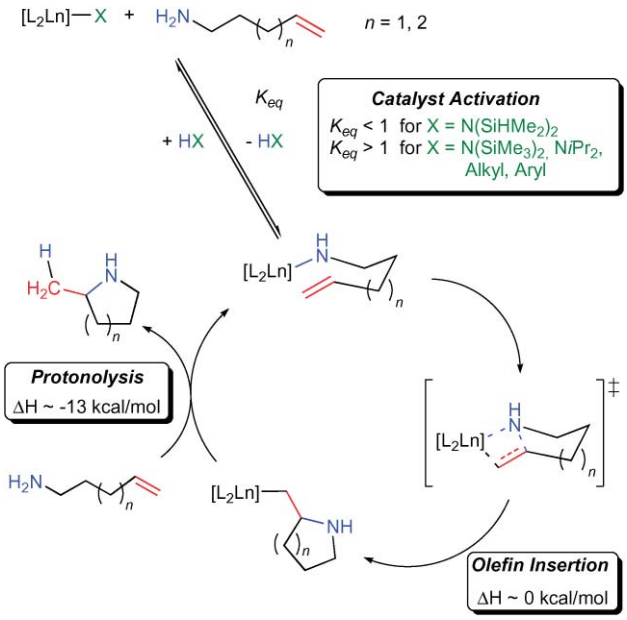
their reduced catalytic performance in the presence of strong coordinating groups (*e.g.* ethers) and incompatibility with protic functional groups (*e.g.* alcohols, acids).

In their seminal work, Marks and co-workers showed that organometallic rare earth metal complexes are particularly suitable for the hydroamination/cyclisation of terminal alkenes, 1,3-dienes, allenes and alkynes.[2h] Internal olefins react under more forcing elevated reaction temperatures.[8] Although most *intra*molecular hydroamination reactions proceed readily at room temperature, *inter*molecular hydroamination reactions are usually more problematic. Rates for the intermolecular process are usually two to three orders of magnitude slower,[9] due to entropic disadvantages and unfavourable competition between strongly binding amines and weakly coordinating olefins.

Common rare earth metal based precatalysts comprise of at least one amido or alkyl ligand which is protolytically substituted for an aminoalkene substrate during the catalyst activation step of the hydroamination/cyclisation (Scheme 1). The key step of the catalytic cycle involves rate-limiting insertion of the olefin into the rare earth metal amido bond in a chair-like transition state.[10] Thus, reactions are usually zero order in substrate concentration and first order in catalyst concentration. Subsequent protonation of the resulting rare earth metal alkyl species by a second amine molecule regenerates the rare earth metal amido species and releases the heterocyclic product.



Scheme 1 Simplified mechanism for rare earth metal catalysed hydroamination/cyclisation.

Asymmetric hydroaminations were first reported in 1992 using C_1-symmetric chiral *ansa*-lanthanocenes (Fig. 1).[11] Cyclisation of aminopentene substrates generated pyrrolidine products in up to 74% ee (Table 1) at low temperatures. Enantioselectivities for piperidines were much less favourable until the 'extended wingspan' catalysts (*S*)-**2** [11c] were introduced recently, which allowed the facile synthesis of enantioenriched (+)-coniine *via* aminodiene cyclisation (Scheme 2).[11e] Although most precatalysts could be prepared in diastereomeric pure form, the catalysts underwent facile epimerisation under the conditions of catalytic hydroamination *via* reversible protolytic cleavage of the metal cyclopentadienyl bond (Scheme 3).[8d,11b–e] Therefore, enantiomeric excess and sense of optical rotation of the cyclised products were independent of the diastereomeric purity of the lanthanocene precatalyst.

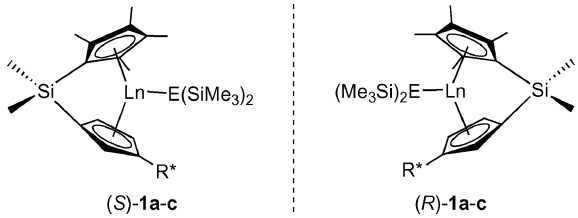
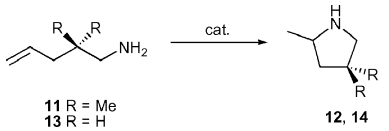


Fig. 1 Chiral lanthanocene precatalysts for asymmetric hydroamination [R* = (+)-neomenthyl (**1a**), (−)-menthyl (**1b**), (−)-phenylmenthyl (**1c**); Ln = La, Nd, Sm, Y, Lu; E = CH, N].

The limitations in enantioselectivity and configurational stability of chiral lanthanocene hydroamination catalysts made the development of catalyst systems based on non-cyclopentadienyl ligand sets imminent. The desired catalyst system should have comparable catalytic activity to the lanthanocene catalyst systems, while allowing a facile catalyst tuning through modular ligand structures in order to achieve efficient enantioselectivities. Furthermore, the catalyst should be prepared conveniently, without the need for elaborate purification techniques, and

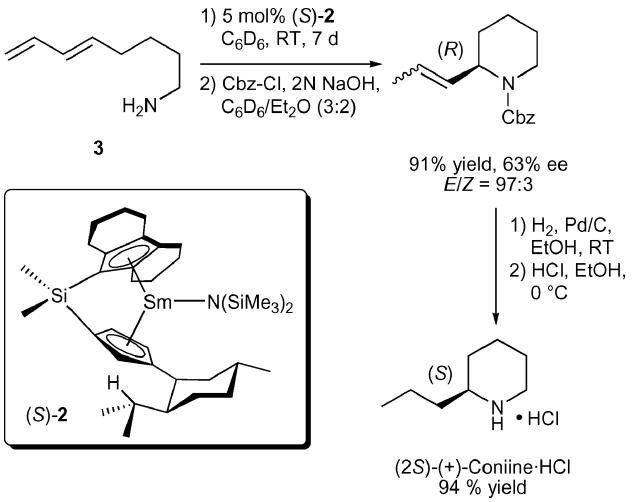
Table 1 Catalytic hydroamination/cyclisation of aminopentenes



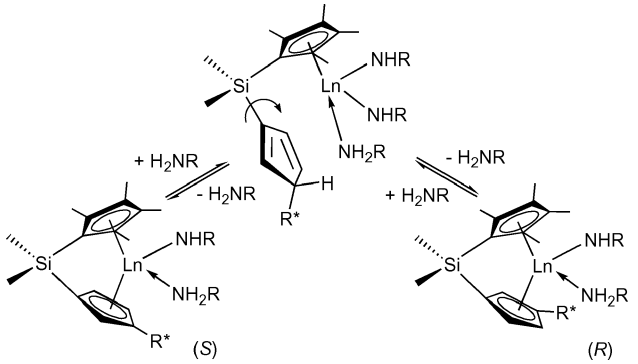
11 R = Me
13 R = H

12, 14

Cat.	Substr.	[cat]/[s] (%)	T/°C	t/h; conv. (%)	TOF/h^{-1}	ee (%) (config.)
(*S*)-**1b-Sm**	**11**		25		84	53 (*S*)
(*S*)-**1b-Sm**	**11**		−30			74 (*S*)
4a	**11**	4	70	22; 77	2.5	36 (*S*)
4b	**11**	2	25	1; 98	61	8 (*S*)
5	**11**	4	60	7; 92	13.5	28.3 (*S*)
6a	**11**	4	22	3; ⩾98	8	43 (*S*)
6b	**11**	4	22	2; ⩾98	14	53 (*S*)
7a	**11**	3	60	336; 100		50
7b	**11**	3	35	120; 100		45
8	**11**	1	70	40; 100		61
9	**11**	5	23	—; >98	25	67 (*R*)
(*S*)-**1b-Sm**	**13**		25		33	62 (*S*)
(*S*)-**1b-Sm**	**13**		0			72 (*S*)
5	**13**	4	70	43; 91		57 (*S*)
6a	**13**	4	22	24; ⩾98	1.2	69 (*S*)
6b	**13**	4	22	20; ⩾98	2.2	83 (*S*)
9	**13**	5	23		0.09	40 (*R*)



Scheme 2 Synthesis of (+)-coniine·HCl *via* enantioselective aminodiene hydroamination/cyclisation (Cbz = benzyloxycarbonyl).



Scheme 3 Epimerisation of chiral lanthanocene complexes during the hydroamination reaction.

should be configurationally stable under the conditions of catalytic hydroamination.

Indeed, several new chiral rare earth metal hydroamination catalysts were introduced recently (Fig. 2, Table 1) utilising various non-metallocene ligand frameworks, such as biphenolate (**4**),[12a,b] binaphtholate (**5** and **6a**,**b**),[12a,c] biaryl diamido (**7a**,**b**),[13a,c] aminophenolate (**8**),[13b] bisoxazolinato (**9**)[14] and diamidobinaphthyl (**10**)[15] ligands.

Catalyst systems **4a**, **5**, **7a** and **8** displayed only low catalytic activity and required elevated reactions temperatures ($\geqslant$60 °C). Here, the low basicity of the $N(SiHMe_2)_2$ ligand hampers catalyst activation (Scheme 1, $K_{eq} < 1$) so that the majority of the precatalyst remains unreactive in the catalytic reaction. Activation of precatalysts having more basic $N(SiMe_3)_2$, $NiPr_2$, alkyl or aryl ligands proceeds more smoothly and significantly better catalyst performance can be observed (Scheme 1, $K_{eq} > 1$). Hence, complexes **4b**, **6a**, **6b** and **9** reached appreciable turnover rates at room temperature, which are of the same order of magnitude observed for lanthanocenes.

The second, more challenging task was tuning the ligand for optimal enantioselectivities and prevention of undesired catalyst aggregation. The biphenolate catalysts **4a**,**b** can serve as illustrative examples: the *tert*-butyl groups are not sterically demanding enough and shield the metal insufficiently. This results in poor enantioselectivities and ready formation of catalytically less active phenolate-bridged dimeric species in the absence of THF.[12a,b] Sterically more demanding 2,6-diisopropylphenyl substituents in the binaphtholate complex **5** effectively prevented these aggregations and enantioselectivities up to 57% ee were obtained. Sterically more demanding tris(aryl)silyl substituents in complexes **6a**,**b** further improved the selectivity. The highest turnover frequencies and enantioselectivities (up to 83% ee) were achieved with the sterically most hindered catalyst **6b**.[12c]

The biaryl diamido complexes **7a** were only moderately selective.[13a] Increasing the denticity of the ligand by introducing *ortho*-anisole substituents on nitrogen did not improve enantioselectivity.[13c] The aminophenolate catalyst **8** was more selective (61% ee for **11**), due to a better 'reach-around' of the chelating aminophenolate ligand.[13b] Shorter linkages between the phenol unit and the biaryl amine resulted in a significantly less selective stereodifferentiation.

The bisoxazolinato compexes **9** displayed ligand accelerated behaviour,[14,16] with maximum rates and highest enantioselectivities observed with a 1 : 1 ligand-to-metal ratio. Variation of the bisoxazoline ligand substitution pattern revealed that an aromatic group in the 4-position and an alkyl or aryl substitution in the 5-position were highly beneficial for catalyst activity and selectivity. A model explaining the observed stereochemistry was proposed based on molecular modelling studies (Fig. 3). Most

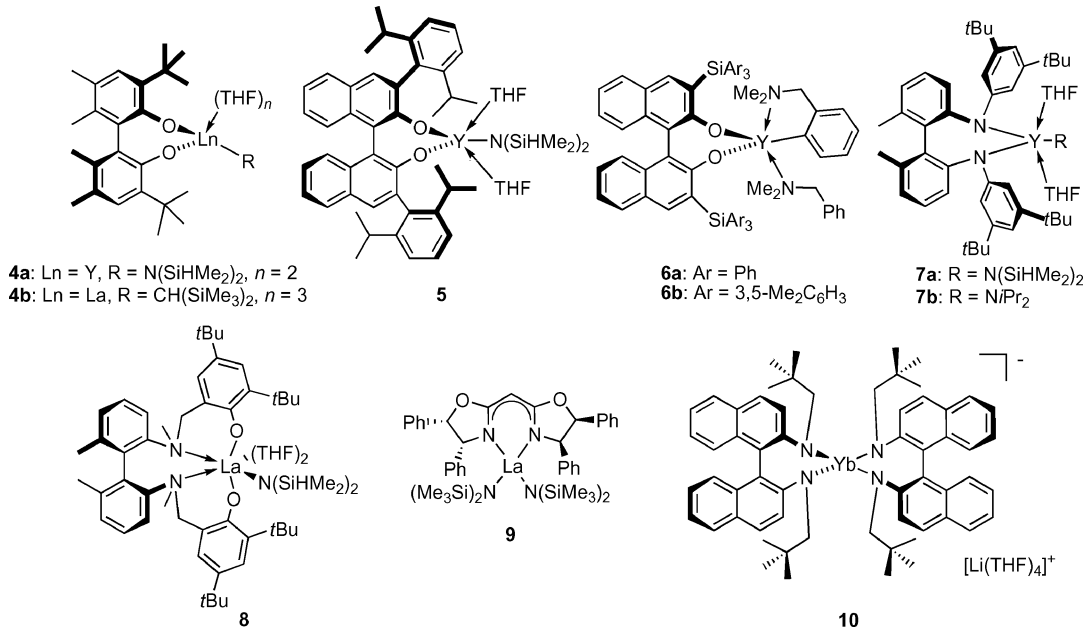
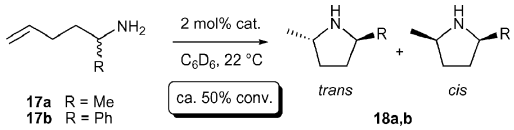


Fig. 2 Chiral, non-metallocene, rare earth metal catalysts for asymmetric hydroamination.

Table 2 Catalytic kinetic resolution of chiral aminopentenes



Cat.	Substr.	*Trans* : *cis*	Conv. (%)	ee of recovered starting material (%)	k_{rel}[a]
6a	**17a**	11 : 1	53	72	9.5
6b	**17a**	13 : 1	52	80	16
6a	**17b**	⩾50 : 1	50	74	15
6b	**17b**	⩾50 : 1	52	63	7[b]

[a] Based on starting material. [b] At 40 °C.

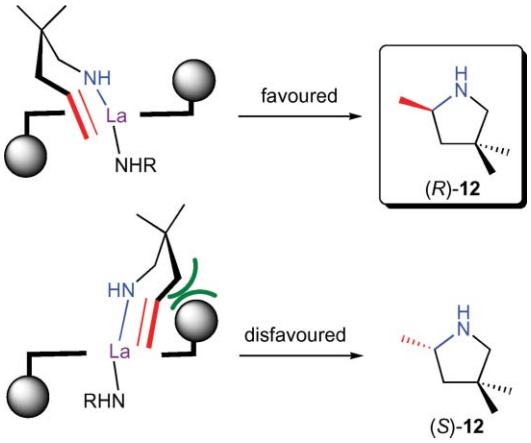
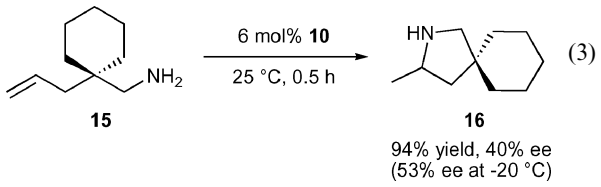


Fig. 3 Stereomodel for enantioselective hydroamination/cyclisation of aminopentene **11** by **9** with an equatorial approach of the olefin.

interestingly, substitution of the aryl group in the 4-position of the ligand for an alkyl substituent led to inversion of product configuration, possibly due to a change in the mode of approach of the olefin to the La–N bond.

The ate-complex **10**[15] is an unusual hydroamination catalyst system as it is the only ate-complex reported to catalyse hydroamination and lacks a reactive amido or alkyl group. It seems feasible that at least one of the diamidobinaphthyl amido groups is protonated, which could ultimately result in loss of one diamidobinaphthyl ligand. Cyclisation of **15**, which is highly activated due to the Thorpe–Ingold effect, to the spirocyclic pyrrolidine **16** proceeded in good activity but with only moderate enantioselectivity [eqn. (3)]. The role of the counter-cation with respect to activity and selectivity is currently unclear.



(3)

Note that there are two opposite trends in the dependence of enantioselectivity on the ionic radius of the metal. For systems based on biphenolate (**4a**,**b**), binaphtholate (**6a**,**b**), biaryl diamido (**7a**), and diamidobinaphthyl (**10**) ligands the selectivity increased with decreasing ionic radius, whereas the opposite was true for aminophenolate (**8**) and bisoxazolinato (**9**) complexes. Chiral lanthanocene complexes (**1** and **2**) on the other hand were most selective with samarium as the central ion.

Kinetic resolution of chiral aminoalkenes

Kinetic resolution processes play a pivotal role in many asymmetric syntheses.[17] Early attempts to perform kinetic resolution of **17a** using chiral lanthanocene complexes were frustrated by low enantiomeric excess (<20% ee) at various extents of conversion.[11b] However, significant higher efficiencies were observed using binaphtholate complexes **6a**,**b** (Table 2) as indicated by k_{rel} values[17] as high as 16.[12c] The 2,5-disubstituted pyrrolidines were obtained in good to excellent *trans* diastereoselectivity, depending on the steric hindrance of the α-substituent. The sterically more hindered binaphtholate catalyst **6b** was more effective in the kinetic resolution of the sterically less demanding **17a**, whereas sterically more encumbered **17b** was more efficiently resolved using the sterically less hindered **6a**.

The preferred formation of (2*S*,5*S*)-**17a** using catalyst **6b** can be explained with an impediment of the cyclisation of (*R*)-**17a** by a sterically unfavourable interaction of the substrate with a trisarylsilyl substituent in the chair-like transition state (Fig. 4).

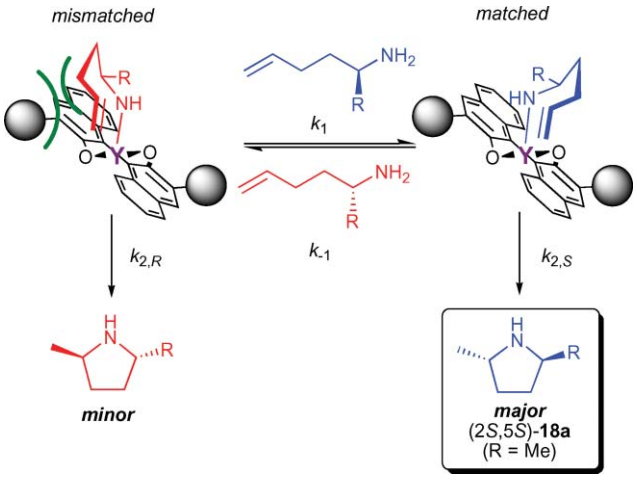


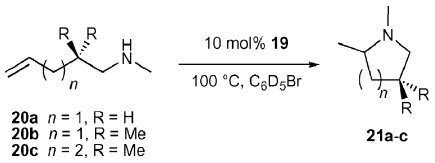
Fig. 4 Proposed stereomodel for the kinetic resolution of chiral aminoalkenes with an equatorial approach of the alkene.

Group 4 metal based catalysts

The application of group 4 metal catalysts in asymmetric hydroamination reactions would be highly desirable as they are easier to prepare and less sensitive than rare earth metal complexes. Their importance in polyolefin synthesis[18] has led to the development of many chiral group 4 metal complexes, some of which are even commercially available.

Unfortunately, neutral group 4 metal complexes are commonly restricted to the catalytic hydroamination of alkynes and

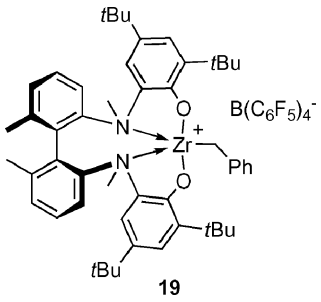
Table 3 Zr-catalysed asymmetric hydroamination/cyclisation of secondary aminoalkenes



Substr.	[cat]/[s] (%)	T/°C	t/h[a]	ee (%)
20a	10	100	4	64
20b	5	70	48	14[b]
20c	10	100	3	82

[a] Time to 100% conversion of substrate. [b] 70% conversion to hydroamination product and 30% double bond isomerised aminoalkene.

allenes only.[2g] The mechanism involves a [2 + 2] cycloaddition of an alkyne or allene to the catalytically active metal imido species, whereas simple alkenes do not react. Although asymmetric cyclisation of aminoallenes to vinylpyrrolidines is possible,[19] the decisive breakthrough was reported by Scott and co-workers using the cationic aminophenolate complex **19**,

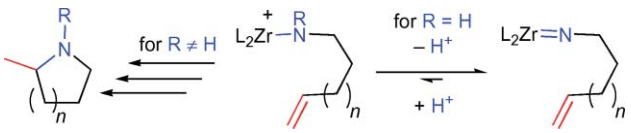


19

which cyclised secondary aminoalkenes with up to 82% ee (Table 3) at 100 °C.[20]

However, cyclisation of **20b** at 70 °C was significantly less enantioselective and partial double bond isomerisation of the starting material was observed.

The mechanism is believed to be similar to that proposed for rare earth metal catalysts, with a catalytically active cationic zirconium amido species. No reaction was observed with primary aminoalkenes, because cationic zirconium amido species are readily deprotonated to yield catalytically inactive zirconium imido species (Scheme 4).



Scheme 4 Reaction pathways for primary and secondary aminoalkenes with cationic zirconium catalysts (n = 1, 2).

Future perspectives

Despite significant recent progress many challenges still lie ahead. So far, only relative simple substrates leading to pyrrolidines and piperidines have been investigated with chiral catalysts, but larger rings and more complex (*e.g.* bicyclic) skeletons are in principle accessible too.[8a,b,9b,21] Another test case will be the application of these systems in intermolecular hydroamination reactions, which might require further catalyst tuning. In spite of the low functional group tolerance and higher air- and moisture-sensitivity of early transition metal catalyst systems, chiral catalyst systems based on late transition metals may be highly desirable, but so far only activated substrates do react.[5,6] The ultimate and final goal, from an atom-economical and cost-efficiency point of view, remains the direct asymmetric hydroamination of non-activated alkenes using ammonia as sole nitrogen source.

Research groups around the globe have accepted the challenge to develop the asymmetric hydroamination into a highly useful catalytic technique in the toolbox for synthetic organic chemists. The payoff for these endeavours will be a facile access to highly valued target compounds starting from simple feed-stocks.

Acknowledgements

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