

Cyclizations

Hydroamination/Cyclization of Aminoalkenes Using Cationic Zirconocene and Titanocene Catalysts***Denis V. Gribkov and Kai C. Hultsch**

Catalytic hydroamination is a highly atom-efficient method for the addition of amines to unsaturated carbon–carbon bonds.^[1] Its relevance to the synthesis of many nitrogen-containing pharmaceuticals and other industrially important basic and fine chemicals has led to intensified research efforts over the last decade, and various catalyst systems based on early and late transition metals have been developed. Catalysts based on rare-earth metals have been proven to be particularly active for the hydroamination of nonactivated olefins.^[1a,2] However, difficulties in the preparation and handling of organo rare earth metal complexes have prevented their widespread application as hydroamination catalysts in synthetic organic chemistry.

Catalyst systems based on Group 4 metal complexes would be more generally applicable due to their easier synthesis and commercial availability.^[3] Unfortunately, catalyst systems based on neutral Group 4 metal complexes have been restricted to inter- and intramolecular hydroamination reactions of alkynes^[1e,f,4] and allenes.^[4b,e] Olefinic substrates are unreactive towards metal imido species, which are presumed to be intermediates in the catalytic cycle.

[*] D. V. Gribkov, Dr. K. C. Hultsch
Institut für Organische Chemie
Friedrich-Alexander Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-852-6865
E-mail: hultsch@chemie.uni-erlangen.de

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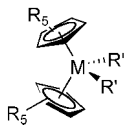


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It should be noted, however, that lanthanocene complexes, which are indeed active hydroamination catalysts, are isoelectronic to alkyl metallocene cations of Group 4 transition metals. While the former have been studied as homogeneous Ziegler–Natta polymerization model systems,^[5] the latter have gained tremendous importance over the last two decades as homogeneous single-site polymerization catalysts.^[6] Alkyl metallocene cations have been used in organic synthesis,^[7] but to the best of our knowledge not in hydroamination reactions. However, Scott et al. recently described the application of a chiral aminophenolate alkyl zirconium cation in asymmetric hydroamination/cyclization reactions.^[8] In this communication we describe the utilization of well-known and readily available alkyl zirconocene cations as competent catalysts for hydroamination/cyclization.

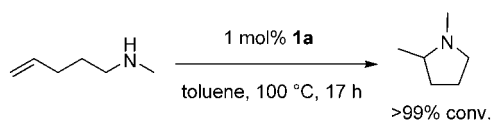
Our initial investigations focused on $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (catalyst system **1a**, Table 1),^[9] and we were

Table 1:



Cat.	M	R	R'	Activator
1a	Zr	H	CH ₃	B(C ₆ F ₅) ₃
1b	Zr	H	CH ₃	[PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻
2a	Zr	CH ₃	CH ₃	B(C ₆ F ₅) ₃
2b	Zr	CH ₃	CH ₃	[PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻
3	Ti	H	CH ₂ Ph	[PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻

pleased to find that it readily cyclizes secondary aminoalkene substrates in aromatic solvents with catalyst loadings as low as 1 mol% (Scheme 1, Table 2 and Table 3). Addition of the



Scheme 1. Cyclization of a secondary aminoalkene substrate with the catalyst $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1a**).

substrates to **1a** at 25 °C results in the immediate release of methane (as observed by ¹H NMR spectroscopy), but appreciable turnover is observed only at elevated temperatures. Cyclization of *N*-methylpent-4-en-1-amine (**4**) proceeds at a rate of $>50 \text{ h}^{-1}$ in [D₅]bromobenzene at 100 °C (Figure 1),^[10] which is roughly 20 times faster than that observed with Scott's catalyst,^[8a] but slower than with $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{NdCH}(\text{SiMe}_3)_2]$ (11 h^{-1} at 25 °C).^[2a] The catalytic activity of **1a** is slightly lower in [D₆]benzene than in [D₅]bromobenzene (Table 2, entries 1 and 2), due to lower solubility of the catalyst in [D₆]benzene.^[11] Formation of α -pipercoline derivative **9** by cyclization of *N*-methylhex-5-en-1-amine (**8**) is significantly slower than formation of pyrrolidine **5**. The sterically more demanding benzyl-substituted aminoalkene **6**

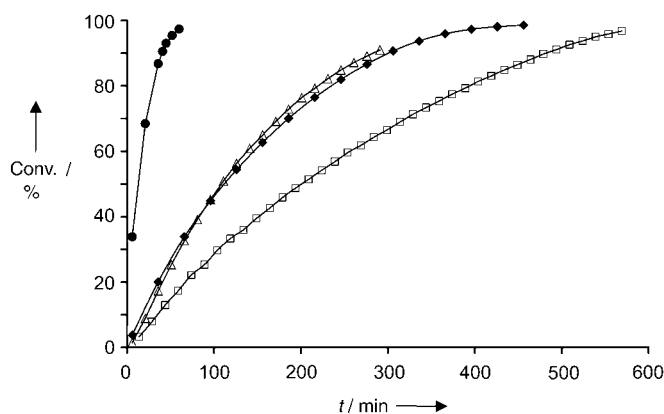
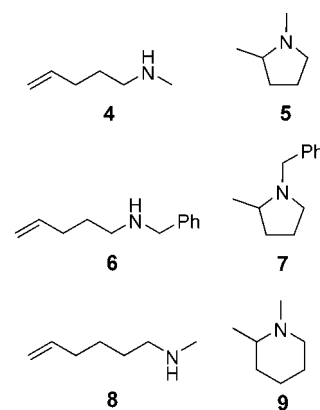


Figure 1. Hydroamination/cyclization of **4** (0.60 M) with 2 mol% of **1a** (\square) at 80 °C in [D₆]benzene, with **1a** (\blacklozenge) at 80 °C in [D₅]bromobenzene, with **1a** (\bullet) at 100 °C in [D₅]bromobenzene, and with **1b** (\triangle) at 80 °C in [D₅]bromobenzene. Lines through the data points are drawn as a guide to the eye.

reacts four times more slowly than the methyl-substituted substrate **4** (Table 2). This seems still sufficient for practical applications, so that the benzyl group could serve as a protecting group for primary aminoalkenes.^[12] In agreement with observations by Scott et al.,^[8a] no catalytic activity was observed for the cyclization of aminoalkenes with primary amine functionalities, for example, 2,2-dimethylpent-4-en-1-amine. The intermediate primary amidozirconocene cation is prone to abstraction of the α -proton from the amido nitrogen atom, leading to a catalytically inactive imidozirconocene species. The catalyst system **1b**, generated by activation of $[\text{Cp}_2\text{ZrMe}_2]$ with $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, performs hydroamination/cyclization reactions with comparable rates for substrates **4** and **10** and higher turnover frequency with benzyl-substituted aminopentene **6** and aminohexene **8**.

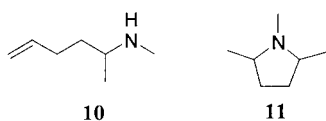
The catalytic activity is very sensitive towards steric hindrance in the coordination sphere of the catalyst. The sterically more encumbered zirconocene $[\text{Cp}_2^*\text{ZrMe}_2]$, activated with either B(C₆F₅)₃ or $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, showed only low activity. Furthermore, the cationic titanocene complex $[\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**3**) has also lower activity than the zirconocene catalysts **1a** and **1b** for most substrates except for substrate **10** (vide infra).

Table 2: Catalytic hydroamination/cyclization reactions of secondary aminoalkenes.^[a]

Entry	S	P	Cat.	[Cat.]/[S] [mol %]	T [°C]	t [h]	Conv. [%] ^[b]	TOF [h ⁻¹] ^[c]
1	4	5	1a	2	80	7	98	12
2	4	5	1a ^[d]	2	80	10	97	6
3	4	5	1a	2	100	1	97	>50
4	4	5	1a ^[e]	1	100	17 ^[f]	>99	
5	4	5	1b	2	80	5	91	12
6	4	5	2a	10	100	74	<10	
7	4	5	2b	10	100	74	11	
8	4	5	3	2	100	218	76	
9	4	5	[Cp ₂ ZrMe ₂] ^[g]	10	100	168	— ^[h]	
10	4	5	[Cp ₂ Ti(CH ₂ Ph) ₂] ^[g]	10	100	20	— ^[i]	
11	4	5	B(C ₆ F ₅) ₃	10	100	24	— ^[h]	
12	6	7	1a	2.5	100	6	94	12
13	6	7	1b	2	100	4	95	24
14	6	7	3	4	100	132	68	
15	8	9	1a	2	100	87	>98	1.6
16	8	9	1b	2	100	12	98	
17	8	9	3	4	100	57	42 ^[j]	

[a] S=substrate, P=product; reaction conditions: 2 mol % cat., [D₅]bromobenzene, Ar atmosphere. [b] Determined by ¹H NMR spectroscopy. [c] Determined from the least-square fit of the linear part of the data. [d] In [D₆]benzene. [e] In toluene. [f] Conditions are not optimized. [g] In [D₈]toluene. [h] No conversion to product observed. [i] Complete isomerization of double bond. [j] No further conversion.

Cyclization of the α -substituted *N*-methyl-*N*-(1-methylpent-4-enyl)amine (**10**) gives *cis*- and *trans*-1,2,5-trimethylpyrrolidines (**11**) with a low *cis/trans* selectivity of 3.3:1 (for



1a) and 3:1 (for **1b**) (Table 3).^[13] The benzyltitanocene cation **3**, on the other hand, shows catalytic activity comparable to that of the zirconocene catalysts but with higher *cis* selectivity (8.6:1 at 80 °C) for substrate **10**. Interestingly, catalyst system **2b**, derived from the permethylzirconocene [Cp₂^{*}ZrMe₂], displays the opposite selectivity of 1:2.

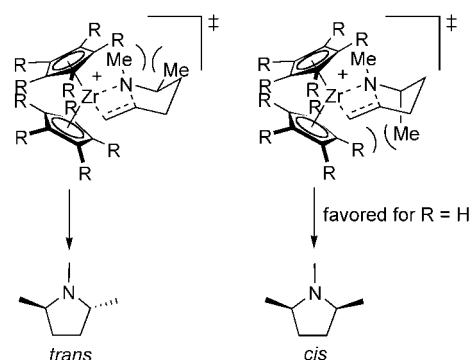
The preferred formation of *cis*-**11** can be rationalized by the unfavorable *gauche* interactions of the *N*-methyl group with the equatorial α -methyl group in the seven-membered

Table 3: Catalytic hydroamination/cyclization of **10** to give **11**.

Entry	Cat. ^[a]	T [°C]	t [h]	Conv. [%] ^[b]	<i>cis:trans</i>
1	1a	80	15	97	3.3:1
2	1a ^[c]	80	21	>99	2.7:1
3	1b	80	27	92	3:1
4	2b ^[d]	100	107	74	1:2
5	3 ^[d]	80	14.5	99	8.6:1
6	3 ^[d]	100	13.5	91	4.9:1

[a] Reaction conditions: 2 mol % cat., C₆D₅Br, Ar atmosphere. [b] Determined by ¹H NMR spectroscopy. [c] In C₆D₆. [d] With 5 mol % cat.

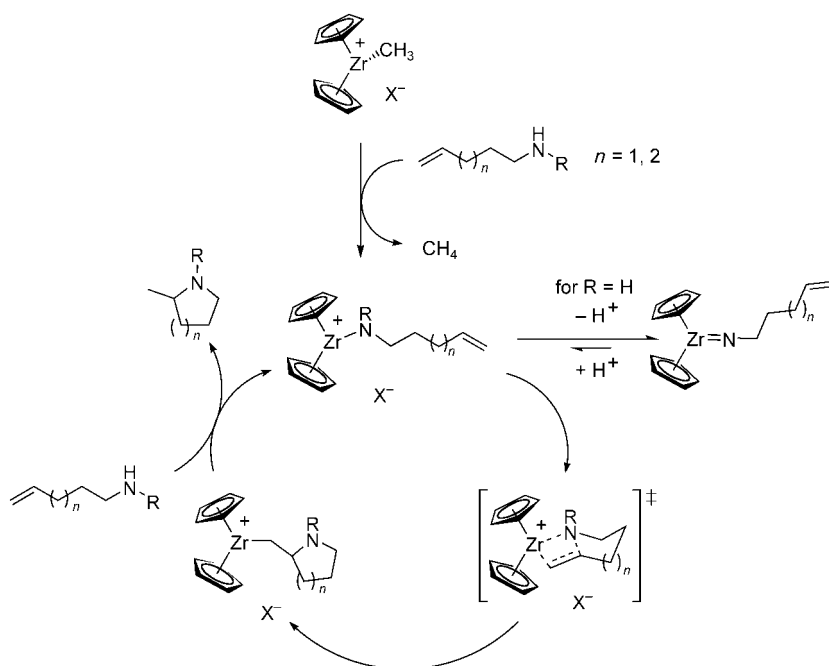
chairlike transition state of the cyclization step leading to the *trans* isomer (Scheme 2). Steric interactions of the axial α -alkyl substituent with the Cp₂^{*} methyl groups in **2b** in the transition state leading to the *cis* isomer would disfavor this reaction path.


Scheme 2. Plausible transition states in the hydroamination/cyclization of *N*-methyl-*N*-(1-methylpent-4-enyl)amine (**10**) yielding *cis*- and *trans*-1,2,5-trimethylpyrrolidines (**11**).

Formation of a cationic species is a fundamental requirement for catalytic activity in the hydroamination of aminoalkenes. The neutral zirconocene [Cp₂ZrMe₂] displayed no catalytic activity after 7 d at 100 °C, whereas titanocene [Cp₂Ti(CH₂Ph)₂] led to complete isomerization of the terminal double bond in substrate **4** within 20 h at 100 °C. Furthermore, the highly Lewis acidic B(C₆F₅)₃ activator was catalytically inactive in the absence of zirconocene initiators.

Although mechanistic details are limited at the moment,^[10] the mechanism of the zirconocene-cation-catalyzed hydroamination/cyclization reaction is thought to be similar to that proposed for rare-earth-metal catalysts,^[2a] involving insertion of the carbon–carbon double bond into the metal amido bond followed by protolytic cleavage of the metal–carbon bond to regenerate the metal amido species (Scheme 3). This mechanism differs significantly from the mechanism for the hydroamination of alkyne substrates observed with neutral Group 4 complexes,^[1e,f] involving cycloaddition of an alkyne to a metal imido species followed by protolytic cleavage of the azametallacyclobutene intermediate.

In summary, the alkyl zirconocene cations **1a** and **1b** are promising and convenient catalysts for the hydroamination/cyclization of secondary aminoalkenes, whereas sterically more encumbered systems and the benzyltitanocene cation **3** show lower catalytic activity. Metallocene precatalysts and borane and anilinium borate activators are commercially available, and the catalysts are easy to handle with standard Schlenk techniques. Current investigations are focusing on the application of chiral metallocene complexes in these hydroamination/cyclization reactions. Topics that need to be addressed include the configurational stability of these chiral systems under catalytic conditions,^[14,15] the influence of steric bulk on catalytic activity, and the potential formation of (η^2 -iminoacyl)metallocene cations by deprotonation of intermediate cationic amido species.^[16]



Scheme 3. Proposed mechanism for zirconocene-catalyzed hydroamination/cyclization of aminoalkenes. $X^- = \text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$, $\text{B}(\text{C}_6\text{F}_5)_4^-$.

Experimental Section

All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glove-box techniques. Metallocene dichlorides (Fluka), $\text{B}(\text{C}_6\text{F}_5)_3$ (Strem), and $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Strem) were used as received. $[\text{Cp}_2\text{ZrMe}_2]$,^[17] $[\text{Cp}_2^*\text{ZrMe}_2]$,^[18] $[\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})_2]$,^[19] and $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1a**),^[9] were synthesized as described in the literature. The substrates were dried by distillation from CaH_2 and stored over molecular sieves.

Representative procedure: **5**-HCl (Table 2, entry 4): In the glove box, a flask was fitted with a stirring bar and was charged with **1a** (8.0 mg, 10.5 μmol) toluene (0.5 mL) and **4** (108 mg, 1.09 mmol). The solution was heated to 100 °C for 17 h. All volatiles were then vacuum-transferred, diluted with diethyl ether (2 mL), and treated with hydrochloric acid (1.2 mL, 1 M in Et_2O , 1.2 mmol) at 0 °C. After 30 min, the suspension was brought to room temperature and the solvent removed in vacuo. The white precipitate was washed with diethyl ether and then dried in air to give 124 mg (84 %) of a white powder. $^1\text{H NMR}$ (300 MHz, D_2O , 25 °C): $\delta = 3.70$ (m, 1H, CH_2N), 3.41 (m, 1H, NCHCH_3), 3.17 (m, 1H, CH_2N), 2.91 (s, 3H, CH_3), 2.36 (m, 1H, $\text{NCH}(\text{CH}_3)\text{CH}_2$), 2.03–2.16 (m, 2H, NCH_2CH_2), 1.75 (m, 1H, $\text{NCH}(\text{CH}_3)\text{CH}_2$), 1.43 ppm (d, $^3J(\text{H,H}) = 6.5$ Hz, 3H, CHCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, D_2O , 25 °C, SiMe_4): $\delta = 66.2$ (NCHCH_3), 56.7 (CH_2N), 39.2 (NCH_3), 31.7 ($\text{NCH}(\text{CH}_3)\text{CH}_2$), 21.5 (NCH_2CH_2), 15.7 ppm (CHCH_3).

Substrates **6**, **8**, and **10** were cyclized by similar procedures.

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