DOI: 10.1002/ejoc.200600115

Neutral Ti Catalysts for the Intramolecular Hydroamination of Alkenes

Carsten Müller,[a] Christian Loos,[a] Nikola Schulenberg,[a] and Sven Doye*[a]

Keywords: Alkenes / Amines / Homogeneous catalysis / Hydroamination / Titanium

Neutral titanium complexes are well known precatalysts for the inter- and intramolecular hydroamination of alkynes. In this publication, we show the capability of several neutral titanium complexes to catalyze intramolecular hydroamination reactions of alkenes. The corresponding pyrrolidine and piperidine products are formed in yields up to 97 %. Among the substrates used, only geminally disubstituted amino alkenes are successfully cyclized.

Introduction

Over the last few years, the hydroamination of alkenes has become a field of intensive research and increasing attention.[1] In principle, the major advantage of this catalytic process is the fact that the reaction takes place without any formation of side products (100% atom efficiency). Furthermore, the desired higher substituted amine products are formed from inexpensive starting materials such as readily available alkenes and simple amines or even ammonia in a single step. As a consequence, the hydroamination of alkenes must be regarded as an environmentally friendly and economically desirable process.

In the past, lanthanide[2] and late-transition metal[3] complexes as well as group-III metal[4] complexes were used most extensively as catalysts for olefin hydroaminations. While group-IV metal catalysts have been used extensively for alkyne hydroaminations,[5] the corresponding Ti- and Zr catalysts for alkene hydroaminations have only been identified recently. Initially, cationic Zr- and Ti catalysts were employed for intramolecular hydroamination reactions of amino alkenes containing a secondary amino group.[6] More recently, Livinghouse et al. and Schafer et al. reported the capability of neutral Zr- and Ti complexes like $Ti(NMe_2)_4$ (**1**) to catalyze intramolecular hydroaminations of amino alkenes containing primary amino groups.[7,8] Based on these reports, we became interested in the question whether the Ti complexes that are used in our group for the hydroamination of alkynes are also suitable catalysts for olefin hydroaminations or not. As the consequence, we investigated the performance of a variety of neutral Ti complexes (**2**–**8**, Figure 1) in intramolecular hydroamination reactions of amino alkenes containing a primary amino group and compared the results with those obtained with $Ti(NMe_2)_4$ (**1**).

[a] Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-54-4205
E-mail: doye@oci.uni-heidelberg.de

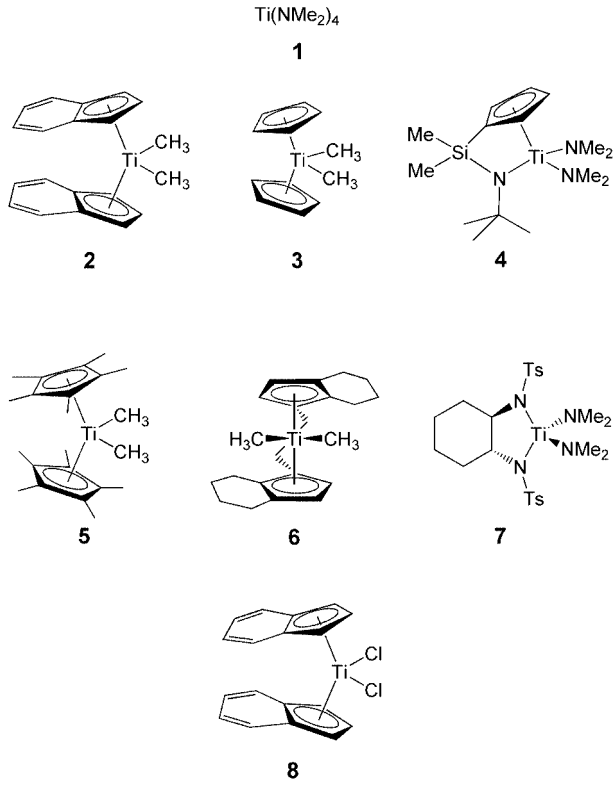


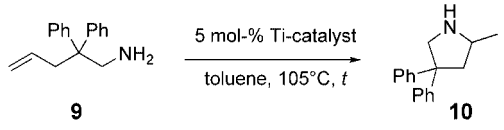
Figure 1. Ti complexes investigated for the intramolecular hydroamination of alkenes.

Results and Discussion

Initial hydroamination experiments were performed with geminally disubstituted 1-amino-2,2-diphenyl-4-pentene (**9**) as starting material. This standard substrate for intramolecular olefin hydroaminations was stirred at 105 °C in toluene in the presence of 5 mol-% of the pre-catalysts **1**–**8** (Figure 1, Table 1). First of all, it can be seen from Table 1 that our results obtained with commercially available $Ti(NMe_2)_4$

(**1**) are comparable to those reported by Schafer et al.[8a] The isolated yields of **10** are 64%, 91%, and 97% after 0.5 h, 1 h, and 24 h reaction time, respectively, and the reaction goes to completion within approximately 1 h (Entries 1–3). Among the other pre-catalysts tested (**2**–**8**), Ind_2TiMe_2 (**2**)[9] was found to be the most active one. Although in this case the reaction needs approximately 15 h to go to completion, the isolated yield after 24 h reaction time is almost as excellent (96%, Entry 9) as obtained with catalyst **1**. With both catalysts, the conversion of **9** to **10** is a very clean reaction, and no side products are observed by GC-MS. In contrast, the formation of a small amount (< 15%) of side products was observed by GC-MS when Cp_2TiMe_2 (**3**)[10] was used as the pre-catalyst. Unfortunately, these side products could only be isolated as an inseparable mixture together with the starting material **9**. However, GC-MS and NMR studies suggest that the side products are probably β-H elimination products formed from **10**. In general, the use of Cp_2TiMe_2 (**3**) results in a relatively slow reaction. Even after 72 h reaction time the reaction does not reach 100% conversion, and the yield of **10** is only 81% (Entry 14). To compare the performance of catalysts **1**–**3**, a plot of isolated yield of **10** vs. the reaction time is shown in Figure 2.

Table 1. Intramolecular hydroamination of amino alkene **9** in the presence of catalysts **1**–**8**.



9 **10**

Entry	Catalyst	*t* [h]	Recovered **9** [%]	Yield **10** [%][a]
1	$Ti(NMe_2)_4$ (**1**)	0.5	33	64
2		1	6	91
3		24	–	97
4	Ind_2TiMe_2 (**2**)	2	63	33
5		4	16	63
6		6	11	84
7		8	8	89
8		15	1	97
9		24	–	96
10	Cp_2TiMe_2 (**3**)	4	57[b]	42
11		6	49[b]	49
12		15	24[b]	75
13		24	11[b]	86
14		72	17[b]	81
15	**4**	24	24	74
16	$Cp^*_2TiMe_2$ (**5**)	24		< 10[c]
17	*S*,*S*-(ETBHI)$TiMe_2$ (**6**)	24	83	12[d]
18	**7**	24		< 5[c]
19	Ind_2TiCl_2 (**8**)	24		< 5[c][e]

[a] Reaction conditions: amino alkene (2.4 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (2.0 mL), 105 °C. Yields refer to isolated pure compounds. [b] Contaminated with a mixture of by-products. [c] Estimated by GC/MS analysis. Neither the product nor the starting material was isolated. [d] The product was obtained with 2% *ee* [GC-MS analysis of the corresponding (*S*)-(–)-*N*-(trifluoroacetyl)prolyl amide]. [e] Triethylamine (0.24 mmol, 10 mol-%) was added to the reaction mixture.

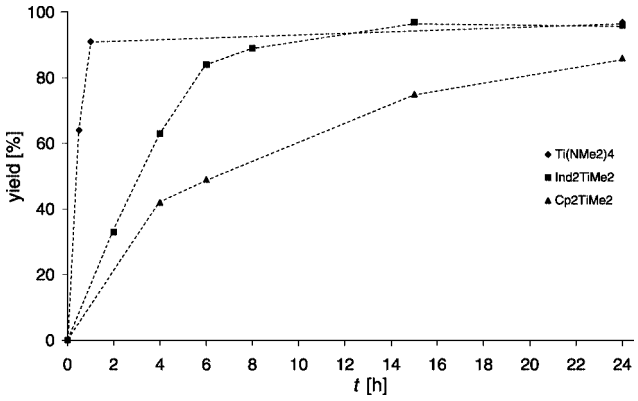
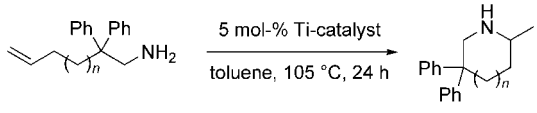


Figure 2. Plot of isolated yield of **10** vs. the reaction time (5 mol-% catalyst, 105 °C).

Subsequent reactions performed with catalysts **4**–**8** (Entries 15–19) revealed that the *ansa* complex **4**[11] is comparable in activity with Cp_2TiMe_2 (**3**), while the catalysts **5**–**8**[12,13] do not catalyze the hydroamination reaction of **9** efficiently. However, the use of catalyst **4** does not lead to the formation of any side products as observed in the case of Cp_2TiMe_2 (**3**).

A slightly different picture was obtained when we tried to synthesize six- and seven-membered rings by hydroamination reactions of substrates **11** and **13** (Table 2).

Table 2. Formation of six- and seven-membered rings by intramolecular hydroamination in the presence of catalysts **1**–**4**.



11: *n* = 1
13: *n* = 2

12: *n* = 1
14: *n* = 2

Entry	Amino alkene	Catalyst	Recovered starting material [%]	Product	Yield [%][a]
1	**11**	$Ti(NMe_2)_4$ (**1**)	15	**12**	76
2		Ind_2TiMe_2 (**2**)	–		89
3		Cp_2TiMe_2 (**3**)	10[b]		78
4		**4**	13		75
5	**13**	$Ti(NMe_2)_4$ (**1**)	94	**14**	–
6		Ind_2TiMe_2 (**2**)	93		–

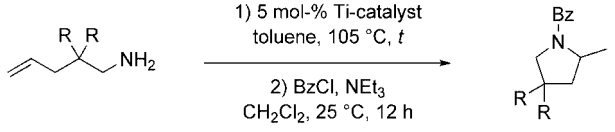
[a] Reaction conditions: amino alkene (2.40 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (2.0 mL), 105 °C, 24 h. Yields refer to isolated pure compounds. [b] Contaminated with a mixture of by-products.

As can be seen from Table 2, the cyclization of **11** to form the piperidine product **12** only goes to completion within 24 h at 105 °C when Ind_2TiMe_2 (**2**) is used as the pre-catalyst. In this case, the isolated yield of **12** is 89% (Entry 2). Surprisingly, the result obtained with pre-catalyst **1** is

slightly worse with respect to conversion (85%) and yield (76%, Entry 1). Even more surprising is the fact that the performance of pre-catalysts Cp_2TiMe_2 (**3**) and **4** is comparable to the performance of **1** (Entries 1, 3, 4). This finding is in sharp contrast to the results obtained for the formation of the pyrrolidine **10**. As described above, the formation of a small amount (<5%) of side products was observed by GC-MS when Cp_2TiMe_2 (**3**) was used as the pre-catalyst. Again, these side products could not be separated from unreacted starting material **11**. Unfortunately, neither $Ti(NMe_2)_4$ (**1**) nor Ind_2TiMe_2 (**2**) were able to catalyze the formation of a seven-membered ring from the amino alkene **13** (Entries 5, 6). Even at elevated temperatures (130 °C, 24 h) no conversion was observed in this case.

Finally, less Thorpe–Ingold-activated 1-amino-4-pentene derivatives **15** and **17** were used as substrates for hydroamination reactions in the presence of the pre-catalysts **1**–**5** (Table 3). Due to the low boiling points of the initial hydroamination products, benzoyl chloride and NEt_3 were added to all crude reaction mixtures obtained from the hydroamination experiments in order to obtain the non-volatile benzamides **16** and **18**. However, only the geminally dimethyl-substituted substrate **15** underwent successful cyclization reactions to finally give **16**. Among the pre-catalysts tested, again $Ti(NMe_2)_4$ (**1**) and Ind_2TiMe_2 (**2**) proved to be the most active ones (Entries 1–4). As expected, the reactions are significantly slower than in the case of geminally diphenyl-substituted substrate **10**. However, after relatively long reaction times (96 h) of the hydroamination reactions the isolated yields of product **16** were 87% and 74%, respectively. In contrast, only trace amounts of product **16** (< 8%) were obtainable with the pre-catalysts **3**, **4** and **5** (Entries 5–10). Unfortunately, unsubstituted 1-amino-4-pentene (**17**) did not undergo cyclization reactions in the presence of the pre-catalysts **1** and **2**. Even at temperatures as high as 150 °C no conversion was observed.

Table 3. Intramolecular hydroamination of less Thorpe–Ingold-activated amino alkenes **15** and **17** in the presence of the catalysts **1**–**5**.



15: R = CH_3
17: R = H

16: R = CH_3
18: R = H

Entry	Amino alkene	Catalyst	*t* [h]	Product	Yield [%][a]
1	**15**	$Ti(NMe_2)_4$ (**1**)	24	**16**	48
2			96		87
3		Ind_2TiMe_2 (**2**)	24		31
4			96		74
5		Cp_2TiMe_2 (**3**)	24		–
6			96		< 5[b]
7		**4**	24		–
8			96		8
9		$Cp^*_2TiMe_2$ (**5**)	24		–
10			96		< 5[b]
11	**17**	$Ti(NMe_2)_4$ (**1**)	96	**18**	–
12		Ind_2TiMe_2 (**2**)	96		–

[a] Reaction conditions: amino alkene (2.4 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (2.0 mL), 105 °C. Yields refer to isolated pure compounds. [b] Estimated by GC/MS analysis. Neither the product nor the benzamide of the starting material was isolated.

Conclusions

In summary, we have presented an initial overview about the activity of eight neutral Ti pre-catalysts in intramolecular hydroaminations of alkenes. Best results for cyclizations to pyrrolidine derivatives were generally obtained with $Ti(NMe_2)_4$ (**1**). In the case of piperidine formation, Cp_2TiMe_2 (**3**) and the *ansa*-catalyst **4** are comparable in activity to **1** and Ind_2TiMe_2 (**2**) seems to be the most active catalyst. While geminally disubstituted amino alkenes are suitable substrates for the hydroamination reactions, an unsubstituted amino alkene did not undergo successful cyclization. However, the presented results clearly indicate that in principle a wide variety of neutral Ti complexes can be used as catalysts for the hydroamination of alkenes. Further studies involving more amino alkene substrates (e.g. 1-amino-2,2,5-triphenyl-4-pentene, 1-amino-5-methyl-2,2-diphenyl-4-pentene, 1-amino-2-phenyl-4-pentene, 1-amino-1-phenyl-4-pentene, etc.) are currently underway in our laboratories. The results will be published as a full paper in this journal in due course.

Experimental Section

General Remarks: All reactions were performed under nitrogen or argon in flame-dried Schlenk tubes (Duran glassware, 100 mL, Ø 30 mm) equipped with Teflon stopcocks and magnetic stirring bars (15 × 4.5 mm). The catalysts were synthesized according to literature procedures (**2**,[9a] **3**,[10a] **4**,[11] **5**,[12a] **7**[12c]) or purchased from Acros Organics (**1**), MCAT[13] (**6**), and Aldrich (**8**). Toluene was distilled from molten sodium or purchased (toluene extra dry with molecular sieves) from Acros Organics. The amino alkenes were synthesized according to literature procedures.[14] 1-Amino-2,2-diphenyl-4-pentene (**9**), 1-amino-2,2-diphenyl-5-hexene (**11**), and 1-amino-2,2-diphenyl-6-heptene (**13**) were purified by kugelrohr distillation. 1-Amino-2,2-dimethyl-4-pentene (**15**) and 1-amino-4-pentene (**17**) were distilled (20 cm vigreux column) from CaH_2 on molecular sieves. All amino alkenes and catalysts except Cp_2TiMe_2 were stored in a nitrogen-filled glovebox (M. Braun). Cp_2TiMe_2 was stored in solution in toluene (c = 0.46 mol/L) under argon at –30 °C. All other compounds were purchased from commercial sources and were used without further purification. Unless otherwise noted, yields refer to isolated yields of pure compounds as gauged by thin-layer chromatography (TLC), ^1H and ^{13}C NMR spectroscopy. All products were characterized by ^1H NMR, ^{13}C NMR, infrared (IR) spectroscopy, and mass spectrometry (MS). Additional characterization data were obtained by CHN elemental analysis. NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer. All ^1H NMR spectra are reported in δ units ppm relative to the signal for $CDCl_3$ at δ = 7.26 ppm or TMS at δ = 0.00 ppm. All ^{13}C NMR spectra are reported in δ units ppm relative to the central line of the triplet for $CDCl_3$ at δ = 77.0 ppm. Infrared spectra were recorded with a Bruker Vector 22 spectrometer using an attenuated total reflection (ATR) method. Mass spectra were

recorded with a JEOL JMS-700 or a Finnigan TSQ 700 (EI) spectrometer with an ionization potential of 70 eV. Elemental analyses were carried out with an Elementar Vario EL machine. GC-MS analyses were performed with a Hewlett–Packard HP 5890 Series II gas chromatograph equipped with a Hewlett Packard HP 5972 Series I Mass Selective Detector. PE: light petroleum ether, b.p. 40–60 °C.

2-Methyl-4,4-diphenylpyrrolidine (10): A flame-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with 1-amino-2,2-diphenyl-4-pentene (**9**) (570 mg, 2.40 mmol), the pre-catalyst (0.12 mmol, 5 mol-%, Table 1), and toluene (2.0 mL). Then, the tube was sealed, and the resulting mixture was heated to 105 °C for the appropriate time (Table 1). After the mixture had been cooled to room temperature, the product **10** was isolated as a colorless oil by flash chromatography (SiO_2, PE/EtOAc, 1:2). For reactions performed with Cp_2TiMe_2 (**3**) as the pre-catalyst, only the amine was added to the Schlenk tube inside of the glovebox. Then, the Schlenk tube was removed from the glovebox and Cp_2TiMe_2 (0.26 mL, c = 0.46 mol/L in toluene, 0.12 mmol, 5 mol-%) and toluene (1.7 mL) were added. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.4 Hz, 3 H), 1.98–2.04 (m, 2 H), 2.70 (dd, J = 12.4, 6.4 Hz, 1 H), 3.30–3.38 (m, 1 H), 3.45 (d, J = 11.4 Hz, 1 H), 3.64 (d, J = 11.4 Hz, 1 H), 7.10–7.14 (m, 2 H), 7.19–7.29 (m, 8 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 22.2 (CH_3), 46.9 (CH_2), 52.9 (CH), 57.1 (C), 57.7 (CH_2), 125.7 (CH), 125.8 (CH), 126.8 (CH), 126.8 (CH), 128.1 (CH), 128.1 (CH), 146.9 (C), 147.6 (C) ppm. IR (neat): $\tilde{\nu}$ = 3084, 3057, 3025, 2958, 2920, 2968, 1598, 1493, 1446, 1372, 1129, 1098, 1032, 906, 869, 773, 756, 700 cm^{-1}. MS (25 °C): m/z (%) = 238 (27) [M + H$^+$], 237 (73) [M$^+$], 222 (8) [M$^+$ – CH_3], 193 (12), 178 (23), 165 (20), 115 (16), 91 (10), 77 (4), 57 (100). $C_{17}H_{19}N$ (237.3): calcd. C 86.03, H 8.07, N 5.90; found C 85.78, H 8.14, N 5.93.

2-Methyl-5,5-diphenylpiperidine (12): A flame-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with 1-amino-2,2-diphenyl-5-hexene (**11**) (603 mg, 2.40 mmol), the pre-catalyst (0.12 mmol, 5 mol-%, Table 2), and toluene (2.0 mL). Then, the tube was sealed, and the resulting mixture was heated to 105 °C for 24 h. After the mixture had been cooled to room temperature, the product **12** was isolated as a colorless oil by flash chromatography (SiO_2, PE/EtOAc, 1:2). For reactions performed with Cp_2TiMe_2 (**3**) as the pre-catalyst, only the amine was added to the Schlenk tube inside of the glovebox. Then, the Schlenk tube was removed from the glovebox and Cp_2TiMe_2 (0.26 mL, c = 0.46 mol/L in toluene, 0.12 mmol, 5 mol-%) and toluene (1.7 mL) were added. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.4 Hz, 3 H), 1.10–1.20 (m, 1 H), 1.29 (br. s, 1 H), 1.60–1.65 (m, 1 H), 2.21 (dt, J = 3.7, 13.4 Hz, 1 H), 2.67–2.81 (m, 2 H), 3.10 (d, J = 13.7 Hz, 1 H), 3.91 (dd, J = 13.7, 3.0 Hz, 1 H), 7.08–7.43 (m, 10 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 22.5 (CH_3), 31.4 (CH_2), 35.4 (CH_2), 45.2 (C), 52.3 (CH), 55.8 (CH_2), 125.7 (CH), 125.7 (CH), 126.4 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 144.8 (C), 148.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 3086, 3057, 3027, 2931, 2864, 2797, 1599, 1494, 1462, 1445, 1376, 1156, 1130, 1107, 925, 844, 751, 699 cm^{-1}. MS (25 °C): m/z (%) = 252 (5) [M + H$^+$], 251 (10) [M$^+$], 236 (5) [M$^+$ – CH_3], 193 (3), 179 (32), 165 (40), 115 (7), 91 (9), 71 (7), 58 (100). $C_{18}H_{21}N$ (251.4): calcd. C 86.01, H 8.42, N 5.57; found C 85.78, H 8.44, N 5.84.

***N*-Benzoyl-2,4,4-trimethylpyrrolidine (16):** A flame-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with 1-amino-2,2-dimethyl-4-pentene (**15**) (272 mg, 2.40 mmol), the pre-catalyst (0.12 mmol, 5 mol-%, Table 3), and toluene (2.0 mL). Then, the tube was sealed and the resulting mixture was heated to 105 °C for the appropriate time (Table 3). After the mixture had been cooled to room temperature, CH_2Cl_2 (5.0 mL), benzoyl chloride (0.3 mL, 2.64 mmol), and NEt_3 (1.0 mL, 7.2 mmol) were added. The resulting mixture was stirred at 25 °C for 12 h. Then, the solution was diluted with Et_2O (30 mL), washed with saturated NH_4Cl solution, and dried with $MgSO_4$. After concentration under vacuum in the presence of celite®, the product **16** was isolated as a colorless oil by flash chromatography (SiO_2, PE/EtOAc, 10:1). For reactions performed with Cp_2TiMe_2 (**3**) as the pre-catalyst, only the amine was added to the Schlenk tube inside of the glovebox. Then, the Schlenk tube was removed from the glovebox and Cp_2TiMe_2 (0.26 mL, c = 0.46 mol/L in toluene, 0.12 mmol, 5 mol-%) and toluene (1.7 mL) were added. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (s, 3 H), 1.04 (s, 3 H), 1.31–1.47 (m, 4 H), 1.93 (dd, J = 11.9, 7.5 Hz, 1 H), 3.10 (d, J = 10.4 Hz, 1 H), 3.29 (d, J = 10.4 Hz, 1 H), 4.30–4.42 (m, 1 H), 7.34–7.42 (m, 3 H), 7.52 (d, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 20.1 (CH_3), 25.3 (CH_3), 25.6 (CH_3), 38.1 (C), 47.4 (CH_2), 52.8 (CH), 62.5 (CH_2), 127.4 (CH), 128.0 (CH), 129.8 (CH), 137.2 (C), 170.0 (C) ppm. IR (neat): $\tilde{\nu}$ = 3059, 3029, 2958, 2928, 2868, 1629, 1603, 1578, 1496, 1465, 1447, 1409, 1372, 1352, 1321, 1290, 1213, 1137, 794, 719, 699 cm^{-1}. MS (25 °C): m/z (%) = MS (25 °C): m/z (%) = 218 (1) [M + H$^+$], 217 (4) [M$^+$], 202 (4), 160 (4), 105 (77), 77 (100), 56 (26), 55 (19), 51 (37), 41 (30), 39 (17). $C_{14}H_{19}NO$ (217.3): calcd. C 77.38, H 8.81, N 6.45; found C 77.07, H 8.67, N 6.49.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Dr. Otto Röhm Gedächtnisstiftung, Darmstadt, for financial support of our research.

[1] For reviews, see: a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703; b) J. J. Brunet, D. Neibecker, in *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, 91–141; c) P. W. Roesky, T. E. Müller, *Angew. Chem.* **2003**, *115*, 2812–2815; *Angew. Chem. Int. Ed.* **2003**, *42*, 2708–2710; d) K. C. Hultzsch, *Adv. Synth. Catal.* **2005**, *347*, 367–391; e) K. C. Hultzsch, *Org. Biomol. Chem.* **2005**, *3*, 1819–1824.

[2] For recent examples of hydroamination catalyzed by lanthanide complexes, see: a) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *Chem. Eur. J.* **2003**, *9*, 4796–4810; b) A. Zulys, T. K. Panda, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2004**, 2584–2585; c) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; d) J.-S. Ryu, T. J. Marks, *J. Org. Chem.* **2004**, *69*, 1038–1052; e) S. Tobisch, *J. Am. Chem. Soc.* **2005**, *127*, 11979–11988.

[3] For recent examples of hydroamination catalyzed by late transition metal complexes, see: a) C. F. Bender, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2005**, *127*, 1070–1071; b) J. Takaya, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 5756–5757; c) D. Karshtedt, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646; d) J.-J. Brunet, N. C. Chu, O. Diallo, *Organometallics* **2005**, *24*, 3104–3110; e) A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem.* **2005**, *117*, 7972–7976; *Angew. Chem. Int. Ed.* **2005**, *44*, 7794–7798.

[4] For recent examples of hydroamination catalyzed by group-III metal complexes, see: a) Y. K. Kim, T. Livinghouse, J. E. Bercaw, *Tetrahedron Lett.* **2001**, *42*, 2933–2935; b) J. Y. Kim, T. Livinghouse, *Angew. Chem.* **2002**, *114*, 3797–3799; *Angew. Chem. Int. Ed.* **2002**, *41*, 3645–3647; c) F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers, L. L. Schafer, *Organometallics*

2004, *23*, 2234–2237; d) J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, *7*, 1737–1739; e) J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, *7*, 4391–4393.

[5] For reviews, see: a) I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2003**, 935–946; b) S. Doye, *Synlett* **2004**, 1653–1672; c) A. Odom, *Dalton Trans.* **2005**, 225–233.

[6] a) P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2004**, 894–895; b) D. V. Gribkov, K. C. Hultzsch, *Angew. Chem.* **2004**, *116*, 5659–5663; *Angew. Chem. Int. Ed.* **2004**, *43*, 5542–5546.

[7] H. Kim, P. H. Lee, T. Livinghouse, *Chem. Commun.* **2005**, 5205–5207.

[8] a) J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer, *Org. Lett.* **2005**, *7*, 1959–1962; $TiCl_4$-catalyzed additions of anilines to norbornene and styrenes are claimed in: b) L. Ackermann, L. T. Kaspar, C. J. Gschrei, *Org. Lett.* **2004**, *6*, 2515–2518; c) L. T. Kaspar, B. Fingerhut, L. Ackermann, *Angew. Chem.* **2005**, *117*, 6126–6128; *Angew. Chem. Int. Ed.* **2005**, *44*, 5972–5974. However, based on a more recent report, it is possible that these additions occur via a simple proton-catalyzed process; d) L. L. Anderson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543.

[9] a) A. Heutling, R. Severin, S. Doye, *Synthesis* **2005**, 1200–1204; b) A. Heutling, F. Pohlki, S. Doye, *Chem. Eur. J.* **2004**, *10*, 3059–3071.

[10] a) N. A. Petasis, in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), John Wiley & Sons, New York, **1995**, vol. 1, 470–473; b) E. Haak, I. Bytschkov, S. Doye, *Angew. Chem.* **1999**, *111*, 3584–3586; *Angew. Chem. Int. Ed.* **1999**, *38*, 3389–3391.

[11] a) P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867–869; b) J. Okuda, *Chem. Ber.* **1990**, *123*, 1649–1651; c) W. A. Herrmann, M. J. A. Morawietz, *J. Organomet. Chem.* **1994**, *482*, 169–181; d) D. W. Carpenetti, L. Kloppenburg, J. T. Kupec, J. L. Petersen, *Organometallics* **1996**, *15*, 1572–1581.

[12] a) J. E. Bercaw, R. H. Marvich, L. G. Bell, H. H. Brintzinger, *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238; b) A. Heutling, S. Doye, *J. Org. Chem.* **2002**, *67*, 1961–1964; c) S. Pritchett, P. Gantzel, P. J. Walsh, *Organometallics* **1999**, *18*, 823–831; d) L. Ackermann, R. G. Bergman, R. N. Loy, *J. Am. Chem. Soc.* **2003**, *125*, 11956–11963; e) A. Heutling, F. Pohlki, I. Bytschkov, S. Doye, *Angew. Chem.* **2005**, *117*, 3011–3013; *Angew. Chem. Int. Ed.* **2005**, *44*, 2951–2954.

[13] www.mcat.de

[14] a) M. R. Gagné, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275–294; b) S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783.

Received: February 9, 2006
Published Online: April 19, 2006

