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## Anti-Markovnikov Hydroamination of Terminal Alkynes**

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Christian G. Hartung, and Matthias Beller*

*Dedicated to Professor Dr. Lutz F. Tietze*
*on the occasion of his 60th birthday*

Imines are of significant importance as intermediates for the synthesis of various amines and carbonyl compounds. In general, the synthesis of imines includes amination of a suitable aldehyde or ketone. A more atom-efficient route is the direct hydroamination of alkynes.[1] This method has the additional advantage that no water is produced as a by-product. Hence, various domino reactions (e.g. direct nucleophilic addition of organometallic reagents) are possible, which do not work in the presence of water.

The homogeneously catalyzed intermolecular hydroamination of alkynes is known to proceed in the presence of Hg and Tl salts,[2] alkali metals (Cs),[3] Ti,[4] Zr,[5] Nd,[6] U, and Th[7] complexes. In addition, complexes of late-transition metals (such as Ru, Pd,[8] and Rh[9]) have been used as catalysts for this transformation. Clearly, catalysts based on cheap and easily available titanium and zirconium complexes offer significant advantages compared to those based on toxic metals (Hg, Tl) or more expensive (U, Th, Ru, Pd, and Rh) complexes.

Recently, important progress in the intermolecular hydroamination of alkynes with titanium complexes was made by Johnson and Bergman[10] and by Doye and co-workers.[4] While the former group developed the modified titanium complex $[Cp(ArNH)(py)Ti{=}NAr]$ (Cp = cyclopentadienyl, py = pyridyl) and used it for the reaction of 2,6-dimethylaniline and diphenylacetylene, the latter group described an efficient and general method for the hydroamination of various internal alkynes using dimethyltitanocene as a catalyst. Bytschkov and Doye showed that the turnover frequency of this catalyst can be enhanced by using microwaves.[4c] Kinetic measurements by Bergman[10] and Doye[11] also established a general mechanism of the dimethyltitanocene-catalyzed intermolecular hydroamination of alkynes. Surprisingly little attention was paid to the hydroamination of terminal alkynes using titanium catalysts,[12] although the regioselective, sequential amination and hydroxylation of compounds that are unsaturated at the terminal position is one of the most challenging goals for industrial catalysis. Herein we report the first example of a titanocene-catalyzed anti-Markovnikov hydroamination of terminal aliphatic alkynes.

Some time ago we started a program on catalytic amination reactions of olefins and alkynes.[13, 9] Inspired by the work of Doye and Bergman, we also recently looked for easily available and stable titanocene complexes. Here, titanocene alkyne complexes of the type $[Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CR)]$ (Rosenthal's catalyst)[14] appeared to be suited as amination catalysts.[15] These complexes ($[Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ **1**[14a] and $[Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CPh]$ **2**[14b]) are easily synthesized by reaction of titanocene dichloride with the corresponding silylated alkyne.

Compared to previously used titanocene precatalysts, the titanacyclopropene complexes **1** and **2** are safe and stable under argon at room temperature for many months in German version. Indeed, hydroamination of internal alkynes (diphenylacetylene, 1-phenylpropyne) with aniline or *tert*-butylamine proceeds in excellent yields in the presence of **1** (81–98 % yield after hydrolysis with HCl, Table 1). As shown in Table 2, different terminal aliphatic alkynes react with *tert*-butylamine with extremely high regioselectivity (> 98 %), in high yields (84–98%), and within a short time (2–24 h), by using 0.5–2.5 mol % of catalyst **1**, to give the imines **4a**–**e** and **5**. Although the reactions proceed smoothly with 0.5 mol % of catalyst, we used 2.5 mol % in general because of the shorter reaction time.

Pleasingly, only the anti-Markovnikov products were obtained, which is explained by the selective formation of the

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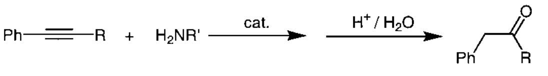
Table 1. Intermolecular hydroamination of internal alkynes in the presence of **1**.[a]

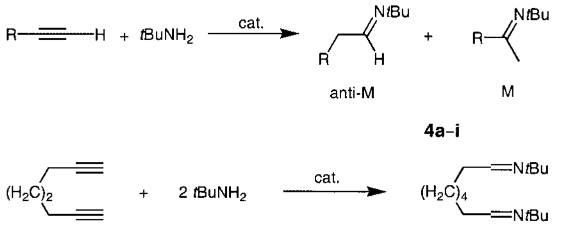


**3a–d**

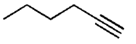
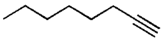
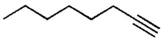
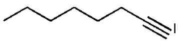
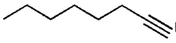
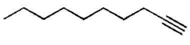
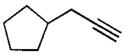
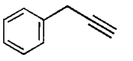
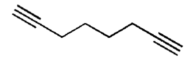
| Alkyne<br>R | Amine<br>R′ | Mole%<br>cat. | $T$<br>[°C] | Conversion<br>[%] | Yield<br>[%][b] |
|---|---|---|---|---|---|
| Ph | $t$Bu | 3.0 | 100 | 100 | 84 (**3a**) |
| Ph | Ph | 3.0 | 140 | 95 | 92 (**3b**) |
| $CH_3$ | $t$Bu | 3.0 | 100 | 100 | 81 (**3c**) |
| $CH_3$ | Ph | 2.0 | 140 | 100 | 98 (**3d**) |

[a] Toluene, 24 h, amine/alkyne = 1.5:1. [b] Determination of yield of the corresponding ketone after hydrolysis of the imine (5% HCl) was by gas chromatography with an internal standard.

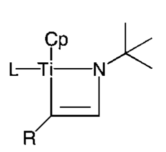
Table 2. Hydroamination of terminal aliphatic alkynes with *tert*-butylamine in the presence of **1**.



**5**

| Entry | Alkyne | Mole%<br>cat. | $T$<br>[°C] | $t$<br>[h] | Amine/<br>Alkyne | Yield [%]<br>(anti-M/M)[a] |
|---|---|---|---|---|---|---|
| 1 |  | 2.5 | 85 | 2 | 1.5:1 | 90 (>99:1) **4a** |
| 2 |  | 2.5 | 85 | 2 | 1.5:1 | 97 (87:1) **4b** |
| 3 |  | 1.0 | 85 | 24 | 1.5:1 | 98 (89:1) **4b** |
| 4 | [b] | 0.5 | 85 | 24 | 1.5:1 | 60 (75:1) **4b** |
| 5 | [c] | 2.5 | 85 | 24 | 1.5:1 | 92 (83:1) **4b** |
| 6 |  | 2.5 | 85 | 24 | 1.5:1 | 93 (63:1) **4c** |
| 7 |  | 2.5 | 85 | 24 | 1.2:1 | 84 (63:1) **4d** |
| 8 |  | 2.5 | 85 | 24 | 1.5:1 | 88 (100:0) **4e** |
| 9 |  | 5.0 | 100 | 2 | 4.0:1 | 92 (100:0) **5** |

[a] GC yield determined with an internal standard (hexadecane or dodecane). [b] 64% conversion. [c] Catalyst: **2**. anti-M/M = anti-Markovnikov/Markovnikov.



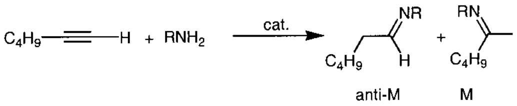
**6**

azatitanacyclobutene **6**. Here, the ligand L represents either another cyclopentadienyl ligand, an amine, or an alkyne, because free cyclopentadiene is observed in most GC spectra of the reaction mixtures.

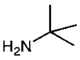
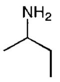
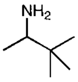
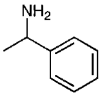
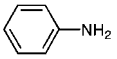
In agreement with the binding constant of the different alkynes, catalyst **1** is slightly more active than catalyst **2** (Table 2, entries 2 and 5). Interestingly, the dihydroamination of diynes, for example, 1,7-octadiyne (entry 9), proceeds smoothly. In the presence of an excess of amine (amine/alkyne = 4:1), both triple bonds react selectively with anti-Markovnikov regiochemistry to yield the 1,8-bisimine **5**. Phenylacetylene also reacts with high regioselectivity to give the anti-Markovnikov product. Unfortunately, a preparative isolation of the corresponding linear imine was not possible because of side reactions during distillation of this product.

Apart from *tert*-butylamine, other aliphatic (*sec*-butylamine, 3,3-dimethyl-2-butylamine), benzylic amines ($\alpha$-methylbenzylamine), and aniline react with 1-hexyne to give imines in high yields (Table 3). Except when using aniline, the anti-Markovnikov products were obtained preferentially. However, the observed regioselectivity is lower than that obtained with *tert*-butylamine, which demonstrates the importance of steric factors for the selective formation of the azatitanacyclobutene **6**. Nevertheless, steric bulk is not the only important factor influencing the regiochemical outcome of the reaction, as shown by the hydroamination of 1-hexyne with aniline.

Table 3. Hydroamination of 1-hexyne with different amines in the presence of **1**.



**4a,f–i**

| Amine | Mole%<br>cat. | $T$ [°C] | $t$ [h] | Amine/<br>Alkyne | Yield [%]<br>(anti-M:M)[a] |
|---|---|---|---|---|---|
|  | 2.5 | 85 | 2 | 1.5:1 | 90 (>99:1) **4a** |
|  | 5.0 | 85 | 24 | 1.5:1 | 86 (3:1) **4f** |
|  | 2.5 | 85 | 24 | 1.5:1 | 96 (4:1) **4g** |
|  | 5.0 | 100 | 24 | 1.2:1 | 79 (2:1) **4h** |
|  | 5.0 | 100 | 24 | 1.2:1 | 94 (1:3) **4i** |

[a] GC yield determined with internal standard (hexadecane or dodecane).

In summary, we have introduced titanocene–alkyne complexes as new catalysts for the hydroamination of internal and terminal alkynes. This class of titanium complexes is easily available, stable, and can be used in a safe and practical manner. The reactions of terminal alkynes with aliphatic amines proceed highly selectively in the presence of catalyst **1** or **2**, to give the corresponding primary anti-Markovnikov functionalized imines in good to excellent yields. Even higher selectivities for anti-Markovnikov aminations might be expected by using sterically more hindered titanocenes.

## *Experimental Section*

Chemicals were obtained from Aldrich, Fluka (solvents), Acros, and Strem and, unless otherwise noted, were used without further purification.

Amines were distilled from $CaH_2$. Alkynes were degassed, flushed with argon, and stored over molecular sieves (4 Å). All experiments were carried out under an argon atmosphere.

Catalysts **1** and **2** were synthesized according to a literature procedure.[14a,b] Imines **4b**–**h** and **5** were isolated after distillation of the crude hydroamination mixtures and were characterized by NMR spectroscopy, MS, IR spectroscopy, and elemental analyses. Identification of all other products was performed by comparison with authentic products. Compounds **4a** and **4i** were synthesized according to the procedures in references [16] and [9], respectively.

Example of a typical hydroamination experiment (**4b**, Table 2, entry 2): A solution of 1-octyne (3.2 mL, 2.4 g, 21.5 mmol) and *tert*-butylamine (3.5 mL, 2.4 g, 32.2 mmol) was treated with **1** (0.15 g, 0.43 mmol, 2 mol %) in toluene (6 mL). This mixture was heated to 85 °C and distilled under vacuum after 24 h. Product **4b** was obtained at 48–49 °C (0.1 mbar); yield: 2.9 g (75 %, >98 % (GC) anti-Markovnikov product); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (t, 3H, $CH_3$), 1.14 (s, 9H, C-$CH_3$), 1.21–1.34 (m, 8H, $CH_2$), 1.46 (m, 2H, $CH_2$), 2.20 (m, 2H, $CH_2$), 7.56 ppm (t, $^3J =$ 5.35 Hz, 1H, CH); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 14.0$ ($CH_3$), 22.6, 26.4, 29.1, 29.2 ($CH_2$), 29.6 (C-$CH_3$), 31.7, 36.4 ($CH_2$), 56.4 ($C_q$), 159.3 ppm (CH); IR (neat): $\tilde{\nu}_{C=N}$: 1671 $cm^{-1}$; MS (EI, 70 eV): $m/z = 184$ $[M^+ + 1]$, 183 $[M^+]$, 168 $[M^+ - CH_3]$, 99 $[C_7H_{15}^+]$, 84 $[C_4H_9NCH^+]$, 57 $[C_4H_9^+]$; elemental analysis $C_{12}H_{25}N$ calcd (%) C 78.62, H 13.74, N 7.64; found C 78.19, H 13.99, N 7.42.

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# Formation of a Butadienenickel-Based Zwitterionic Single-Component Catalyst for Ethylene Polymerization: An Alternative Activation Pathway for Homogeneous Ziegler–Natta Catalysts of Late Transition Metals[**]

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Homogeneous Ziegler–Natta catalysis has become very important in recent years.[1] In addition to the many reported catalysts based on metallocenes with metals from Group 4 and related systems, a variety of Ziegler–Natta systems of late

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[+] X-ray crystal structure analysis.

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