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Zirconium-Catalyzed Intermolecular Hydroamination of Alkynes with Primary Amines

Karolin Born[a] and Sven Doye*[a]

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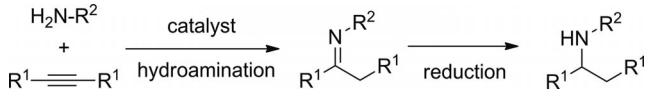
A simple catalyst system generated in situ by combination of 5 mol-% [$Zr(NMe_2)_4$] and 10 mol-% of a sulfonamide catalyzes the intermolecular hydroamination of alkynes with primary amines. At elevated temperatures, hydroamination is achieved with both internal and terminal alkynes as well as with sterically demanding and less demanding primary amines. In contrast, secondary amines do not react under identical conditions. Of the sulfonamide additives investigated, sterically demanding tosylamides such as *N*-(*tert*-butyl)-*p*-toluenesulfonamide give the best results. The regioselectivity of the addition of amine to unsymmetrically substituted internal as well as terminal alkynes is significantly influenced by the nature of the sulfonamide additive. In particular, the successful use of sterically less demanding primary amines such as *n*-hexyl- or benzylamine clearly indicates that the assumption that Zr catalysts generally form catalytically inactive bridging μ^2-imido dimers or other unreactive intermediates in the presence of these amines is not correct.

Introduction

During the last two decades, the hydroamination of alkynes has become a powerful synthetic tool in organic chemistry.[1] If primary amines are used as substrates, this addition reaction results in the direct formation of more or less reactive enamines or imines. Although these initial products can be used in a number of synthetically useful transformations, in most cases they are simply reduced to stable secondary amines (Scheme 1). As a result, the combination of an initial hydroamination of an alkyne and a subsequent reduction in one pot has turned out to be a highly efficient protocol for the synthesis of secondary amines from alkynes and primary amines.



Scheme 1. Alkyne hydroamination/reduction sequence for the synthesis of secondary amines from alkynes and primary amines.

One of the most influential papers published in the field of hydroamination chemistry appeared almost 20 years ago.[2a] Therein, Walsh, Baranger, and Bergman reported the first example of a zirconium complex that catalyzes the intermolecular hydroamination of alkynes.[2] Unfortunately, with this zirconocene catalyst, [$Cp_2Zr(NH\text{-}2,6\text{-}Me_2C_6H_3)_2$], which is converted into a catalytically active zirconium-imido complex under the reaction conditions, it was only possible to use a single amine substrate, namely the sterically demanding primary amine 2,6-dimethylaniline. This severe disadvantage was overcome when our group found in 1999 that closely related titanium catalysts such as [Cp_2TiMe_2] catalyze the addition of a large number of primary aryl- and alkylamines to many alkynes.[3] Since then, the Ti-catalyzed addition of primary amines to alkynes has been investigated in detail by many groups around the world[1c,4] and today it is regarded as a reliable and powerful tool in organic chemistry that is even mentioned in undergraduate text books.[5] Although tetracoordinated titanium complexes are used as catalyst precursors in most cases, it is generally accepted that titanium-imido complexes possessing a Ti=N double bond are the catalytically active species. These highly reactive metal complexes undergo C–N bond-forming [2+2] cycloaddition reactions with the employed alkyne substrates yielding azatitanacyclobutenes. Subsequent protonation of the titanium–carbon bond by excess amine and α-elimination of the hydroamination products regenerate the catalytically active imido complexes.[6] Because the formation of titanium-imido complexes is essential for successful alkyne hydroamination the reaction is limited to primary amines. In addition, the presence of at least two labile ligands at the titanium center that can undergo protonolysis with the primary amine to form the imido moiety is required. One major problem of the hydroamination reactions mentioned above is the ability of the catalytically active zirconium- or titanium-imido complexes to undergo dimerization reactions that result in the

[a] Institut für Reine und Angewandte Chemie, Universität Oldenburg,
Carl-von-Ossietzky-Str. 9–11, 26111 Oldenburg, Germany
Fax: +49-441-798-3329
E-mail: doye@uni-oldenburg.de
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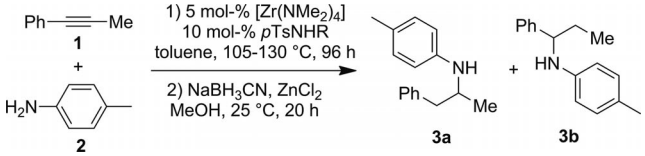
formation of catalytically inactive bridging μ^2-imido dimers. Although the dimerization seems to be reversible with titanium-imido complexes,[6] zirconium-imido complexes with nitrogen substituents that are sterically less demanding than the 2,6-dimethylphenyl group are expected to dimerize irreversibly.[7] This difference in reactivity, which is mainly caused by the different sizes of the titanium and zirconium atoms, has been used as one simple explanation[1c] for the superior performance of titanium catalysts in intermolecular alkyne hydroamination reactions. It also explains why successful intermolecular Zr-catalyzed addition reactions involving alkynes and primary amines that are sterically less demanding than 2,6-dimethylaniline are still extremely rare.[2,8] To the best of our knowledge, only one report exists that describes the very slow addition reactions of aniline and ethylamine to (trimethylsilyl)acetylene (reaction times: 9 and 20 d at 110 °C). Interestingly, these reactions were achieved with 10 mol-% of a Zr catalyst that possesses three ancillary ligands and only one labile amido group. For this reason, this catalyst is expected not to generate an imido species under the reaction conditions.[8] However, another possible explanation for the poor catalytic performance of zirconium catalysts in intermolecular alkyne hydroamination is that azametallacycle formation between sterically less demanding zirconium-imido complexes and alkyne substrates results in very stable intermediates that are either sluggish or unreactive in terms of catalytic turnover.

A significant improvement in the field of group 4 metal-catalyzed hydroamination chemistry was the finding that Ti complexes are also able to catalyze the intramolecular hydroamination of alkenes.[9] Although a large number of suitable Ti catalysts could be identified for the cyclization of aminoalkenes,[10] it turned out that in this case, Zr catalysts are catalytically far more active,[11] a finding that is in sharp contrast to the behavior in alkyne hydroamination. Particularly interesting is the fact that the cyclization of primary aminoalkenes performed with zirconium catalysts does not require the presence of a sterically crowded amino group. Clearly, in this case irreversible dimerization of in situ generated zirconium-imido complexes or the formation of stable intermediates does not represent a problem at all. Although the majority of Ti and Zr catalysts only allow the cyclization of aminoalkene substrates possessing primary amino groups, there are a few examples of catalysts that also allow cyclization reactions of secondary aminoalkenes.[12,13] This finding led to an ongoing extensive discussion about the mechanism of the group 4 metal-catalyzed intramolecular hydroamination of alkenes because metal-imido complexes cannot be formed from titanium or zirconium catalyst precursors and secondary amines. As a consequence, metal-imido complexes cannot be the catalytically active species in hydroamination reactions performed with secondary amines. Consequently, an alternative mechanism for the Zr-catalyzed intramolecular hydroamination of alkenes has recently been proposed by Stubbert and Marks.[13] In analogy to rare-earth-metal-catalyzed hydroamination reactions,[14] it is suggested that zirconium-amido complexes are the catalytically active species, which can undergo alkene insertion into the metal–nitrogen bond in the C–N bond-forming reaction. This suggestion was recently supported by the finding of Schafer and co-workers that bis(ureate)-zirconium complexes also catalyze the intermolecular hydroamination of alkynes with secondary amines.[12b] The insertion mechanism would also explain why primary aminoalkenes with sterically less demanding NH_2 groups are suitable substrates for Zr-catalyzed intramolecular hydroamination because it does not rely on the formation of imido intermediates, which are supposed to undergo irreversible dimerization. In respect of the various experimental results and the ongoing discussion of the mechanism, we thought it would be helpful to find out whether zirconium catalysts can also be used for efficient intermolecular addition of sterically less demanding primary amines to alkynes or not. To answer this question we herein report the use of $[Zr(NMe_2)_4]$ in conjunction with sulfonamides as a successful catalyst system in the intermolecular alkyne hydroamination with a number of primary amines including aryl- and alkylamines as well as sterically less demanding amines. Of the sulfonamides investigated, sterically demanding tosylamides gave the best results.

Results and Discussion

Initially, to support the expectation that simple zirconium catalysts are not able to catalyze the intermolecular addition of sterically less demanding primary amines to alkynes we performed hydroamination experiments with 1-phenylpropyne (**1**) and *p*-toluidine (**2**) at 105 and 130 °C in toluene in the presence of 5 mol-% of commercially available $[Zr(NMe_2)_4]$ (Table 1, entries 1 and 2). As expected,

Table 1. Hydroamination/reduction sequence performed with 1-phenylpropyne (**1**) and *p*-toluidine (**2**).



Entry	Sulfonamide	*T* [°C]	Yield [%][a,b]	**3a/3b**[c]
1	–	105	<1	–
2	–	130	<1	–
3	**4**	105	<1	–
4	**4**	130	<1	–
5	**5**	105	7	87:13
6	**5**	130	74	86:14
7	**6**	105	13	95:5
8	**6**	130	72	88:12
9	**7**	130	84	90:10
10	**8**	130	46	92:8
11	**9**	130	<1	–

[a] Reaction conditions: 1) Alkyne **1** (2.0 mmol), amine **2** (2.2 mmol), $[Zr(NMe_2)_4]$ (0.1 mmol, 5 mol-%), sulfonamide (0.2 mmol, 10 mol-%), toluene (2 mL), 105 or 130 °C, 96 h; 2) $NaBH_3CN$ (4.0 mmol), $ZnCl_2$ (2.0 mmol), MeOH (10 mL), 25 °C, 20 h. [b] Yields refer to isolated compounds. [c] Determined by GC prior to chromatography.

even after a long reaction time of 96 h and a subsequent reduction step ($NaBH_3CN$, $ZnCl_2$, MeOH, 25 °C, 20 h) it was not possible to detect either of the potential products **3a** or **3b** in the crude reaction mixtures. Thus, in subsequent hydroamination experiments we generated a number of zirconium catalysts in situ by combining 5 mol-% [Zr(NMe_2)$_4$] and 10 mol-% of a sulfonamide (**4**–**9**, Figure 1) in toluene and stirring the mixture at room temperature for 2 h prior to the addition of substrates **1** and **2**. After heating the resulting reaction mixtures (105 or 130 °C) for 96 h and subsequent reduction the products **3a** and **3b** were formed in a number of cases. Of the sulfonamides tested, the sterically more demanding derivatives **5**–**8** gave the best results (Table 1, entries 5–10) whereas the sterically less demanding sulfonamides **4** and **9** turned out to be poor additives (Table 1, entries 3, 4, and 11). Overall, a maximum yield of 84% of the desired mixture of products **3a** and **3b** was obtained with *N*-(cyclohexyl)-*p*-toluenesulfonamide (**7**) at a reaction temperature of 130 °C for the hydroamination step. In addition, good yields of 74 and 72% were obtained under identical conditions with *tert*-butyl- and *p*-methoxyphenyl-substituted *p*-toluenesulfonamides **5** and **6**, respectively. As expected for a group 4 metal-catalyzed hydroamination of a 1-aryl-2-alkylalkyne the anti-Markovnikov product **3a** was always the major product of the reaction.[1b,1c] However, note that the regioselectivity of the addition reaction, which is usually around 90:10, is significantly influenced by the structure of the added sulfonamide.

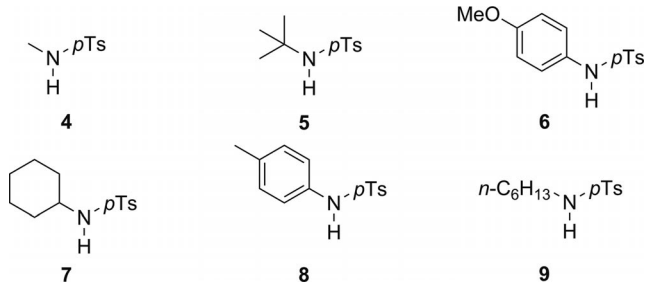


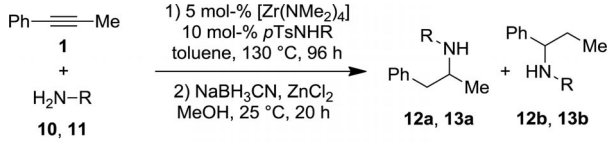
Figure 1. Sulfonamides used as additives in the Zr-catalyzed intermolecular hydroamination of alkynes.

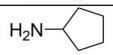
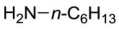
Interestingly, additional reaction sequences performed with a 1:1 or 1:3 ratio of [Zr(NMe_2)$_4$] and the sulfonamide **5** as the catalyst system did not lead to improved results. For example, a mixture of 5 mol-% [Zr(NMe_2)$_4$] and 5 mol-% of **5** delivered the products **3a** and **3b** in a yield of only 53%, which is significantly lower than the yield of 74% obtained with the 1:2 mixture (Table 1, entry 6). Neither was the yield improved with a 1:3 mixture (69% isolated yield); in this case unreacted sulfonamide **5** was detected in the crude product by GC analysis, which was not the case when a 1:2 mixture was used. To acquire some preliminary information about the structures of the species formed in the reactions between sulfonamides and [Zr(NMe_2)$_4$], in situ NMR studies were performed with mixtures of sulfonamide **5** and [Zr(NMe_2)$_4$] in C_6D_6 with ferrocene (δ = 4.00 ppm) as an internal standard. The addition of 1 equiv. of **5** to a solution of [Zr(NMe_2)$_4$] at room temperature led to the slow disappearance (within 2 h) of the NMe_2 signal (singlet at δ = 2.98 ppm) of [Zr(NMe_2)$_4$]. During the reaction a new doublet at δ = 2.17 ppm, which can be assigned to dimethylamine, and a new NMe_2 signal (singlet) shifted downfield to 3.13 ppm appeared. In addition, the signal of the *tert*-butyl group of **5** (singlet at δ = 1.03 ppm) disappeared and a new singlet appeared at δ = 1.27 ppm. Integration of the new NMe_2 and *t*Bu signals at δ = 3.13 and 1.27 ppm suggested that one *t*Bu group and three NMe_2 groups are present in the newly formed species. This finding is in agreement with the formation of the mono-sulfonamide zirconium species [(*t*BuN*p*Ts)Zr(NMe_2)$_3$] from a 1:1 mixture of [Zr(NMe_2)$_4$] and **5**. Importantly, this species could only be detected as a minor compound in the experiment with a 1:2 mixture of [Zr(NMe_2)$_4$] and **5**. In this case, a new NMe_2 signal (broad singlet) appeared at δ = 3.35 ppm together with the signal of dimethylamine (in this experiment, a broad singlet at δ = 2.21 ppm). Integration of these two signals supported the expectation that 2 equiv. of dimethylamine are formed with two NMe_2 groups remaining bonded to the Zr center. Integration of the new NMe_2 signal at δ = 3.35 ppm relative to the new signal for the *t*Bu group at δ = 1.31 ppm is in agreement with the presence of two *t*Bu groups and two NMe_2 groups. Although these data strongly suggest the formation of a bis-sulfonamido zirconium species [(*t*BuN*p*Ts)$_2$Zr(NMe_2)$_2$], we believe that the broadened signals do not allow the unequivocal confirmation of this structure. Because the broad signals may be caused by ligand-exchange processes it cannot be excluded that other species are present in the mixture.

With these promising results in hand, we turned our attention towards the corresponding reactions of 1-phenylpropyne (**1**) with cyclopentylamine (**10**) and *n*-hexylamine (**11**; Table 2). These hydroamination reactions were also successful in toluene at 130 °C in the presence of catalyst systems generated in situ from mixtures of 5 mol-% [Zr(NMe_2)$_4$] and 10 mol-% of one of the sulfonamides **5**–**9**. After a reaction time of 96 h and subsequent reduction, the desired products were obtained as mixtures of regioisomers in moderate yields. With regard to the overall yield, the best results were obtained with the sterically demanding *N*-(*tert*-butyl)-*p*-toluenesulfonamide (**5**). Unfortunately, with this additive the regioselectivities of the hydroamination step were poor, ranging between 50:50 and 53:47. Although better regioselectivities of up to 87:13 were observed with other sulfonamide additives it should be noted that the corresponding Ti-catalyzed processes generally gave much better regioselectivities.[15]

Once we had established that hydroamination reactions of 1-phenylpropyne (**1**) could be achieved with various primary amines using in situ generated mixtures of [Zr(NMe_2)$_4$] and sulfonamides, we examined the reactions of the sterically more demanding alkyne diphenylacetylene (**14**). In this study we recognized that good results could not be obtained when the hydroamination reactions were performed at 130 °C. However, an increase in temperature to 160 °C led to much better results (Table 3). After a reac-

Table 2. Hydroamination/reduction sequences performed with 1-phenylpropyne (**1**) and amines **10** and **11**.



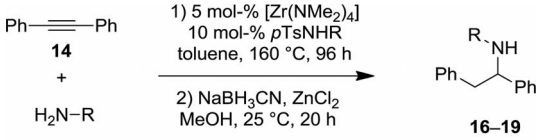
Entry	Amine	Sulfonamide	Product	Yield [%][a,b]	Ratio **a**/**b**[c]
1	 **10**	–	**12a**/**b**	<1	–
2		5		65	53:47
3		6		7	80:20
4		7		<1	–
5		8		23	82:18
6		9		37	73:27
7	 **11**	–	**13a**/**b**	<1	–
8		5		46	50:50
9		6		33	87:13
10		7		48	63:37
11		8		19	85:15
12		9		<1	–

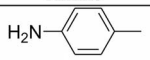
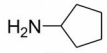
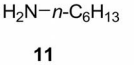
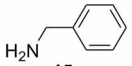
[a] Reaction conditions: 1) Alkyne **1** (2.0 mmol), amine (2.2 mmol), $[Zr(NMe_2)_4]$ (0.1 mmol, 5 mol-%), sulfonamide (0.2 mmol, 10 mol-%), toluene (2 mL), 130 °C, 96 h; 2) $NaBH_3CN$ (4.0 mmol), $ZnCl_2$ (2.0 mmol), MeOH (10 mL), 25 °C, 20 h. [b] Yields refer to isolated compounds. [c] Determined by GC prior to chromatography.

tion time of 96 h it was possible to achieve successful addition reactions of *p*-toluidine (**2**), cyclopentylamine (**10**), *n*-hexylamine (**11**), and benzylamine (**15**) with **14**. Although, the desired secondary amines **16**–**18** were obtained in modest-to-very-good yields with most of the sulfonamides employed (**5**–**9**), the best results were observed with the sterically demanding *N*-(*tert*-butyl)-*p*-toluenesulfonamide (**5**). Most impressively, with this additive, the hydroamination/reduction sequence performed with the sterically less demanding *n*-hexylamine (**11**) gave the product **18** in 93% yield. The superior suitability of the *N*-(*tert*-butyl)sulfonamide **5** as an additive for the Zr-catalyzed hydroamination step is additionally supported by the fact that a successful reaction between diphenylacetylene (**14**) and benzylamine (**15**) could only be achieved with **5** (Table 3, entry 20). Particularly surprising is the fact that one of the hydroamination reactions, namely the addition of *p*-toluidine (**2**) to **14**, could also be achieved in the absence of sulfonamide (Table 3, entry 1). However, the yield of the reaction sequence was only moderate.

In addition to the *p*-toluenesulfonamide derivatives **4**–**9**, we also studied a number of other *N*-(*tert*-butyl)sulfonamides. For this purpose, the methylsulfonyl (**20**), *p*-trifluoromethylphenylsulfonyl (**21**), and *p*-methoxyphenylsulfonyl (**22**) derivatives were used as alternative additives in the hydroamination/reduction sequence of diphenylacetylene (**14**) and *p*-toluidine (**2**) under the already established conditions (Table 4). In this study the sterically less demanding methanesulfonamide **20** gave a poor yield (Table 4, entry 2), whereas the three bulkier aromatic sulfonamides **5**, **21**, and **22** led to the isolation of the product **16** in high yields (82–90%). A comparison of the results

Table 3. Hydroamination/reduction sequence performed with diphenylacetylene (**14**) and various amines.



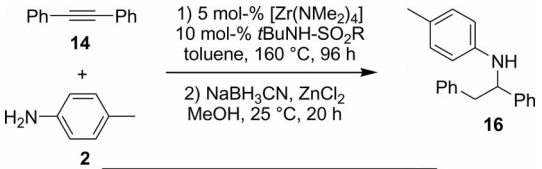
Entry	Amine	Sulfonamide	Product	Yield [%][a,b]
1	 **2**	–	16	46
2		**5**		87
3		**6**		55
4		**7**		70
5		**8**		81
6		**9**		53
7	 **10**	–	17	<1
8		**5**		70
9		**6**		10
10		**7**		26
11		**8**		77
12		**9**		55
13	 **11**	–	18	<1
14		**5**		93
15		**6**		44
16		**7**		64
17		**8**		65
18		**9**		<1
19	 **15**	–	19	<1
20		**5**		68

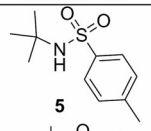
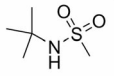
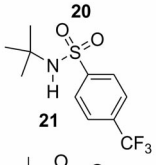
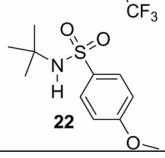
[a] Reaction conditions: 1) Alkyne **14** (2.0 mmol), amine (2.2 mmol), $[Zr(NMe_2)_4]$ (0.1 mmol, 5 mol-%), sulfonamide (0.2 mmol, 10 mol-%), toluene (2 mL), 160 °C, 96 h; 2) $NaBH_3CN$ (4.0 mmol), $ZnCl_2$ (2.0 mmol), MeOH (10 mL), 25 °C, 20 h. [b] Yields refer to isolated pure compounds.

obtained with these last three sulfonamides clearly indicates that these additives do not differ significantly in their catalytic performance. Thus, one can conclude that the electronic properties of the sulfonamide are less important for the catalytic performance than its size.

We next turned our attention towards the reactions of terminal alkynes 1-octyne (**23**) and phenylacetylene (**25**). The hydroamination reactions were performed with *p*-toluidine (**2**) and 5 mol-% $[Zr(NMe_2)_4]$ either in the presence or absence of 10 mol-% sulfonamide **5** (Scheme 2). Because terminal alkynes are known to undergo hydroamination reactions under much milder conditions than internal alkynes,[15] the hydroamination step was always performed at 105 °C. After a relatively short reaction time of 24 h and subsequent reduction it was possible in all cases to isolate the desired secondary amines in modest yields. Particularly interesting is the fact that addition of a sulfonamide to the reaction mixture is not necessary for successful hydroamination reactions. Note, however, that the sulfonamide additive significantly influences the regioselectivity of the hydroamination. For example, the Markovnikov regioisomer **24b** was obtained almost exclusively (**24a**/**24b** = 4:96) from

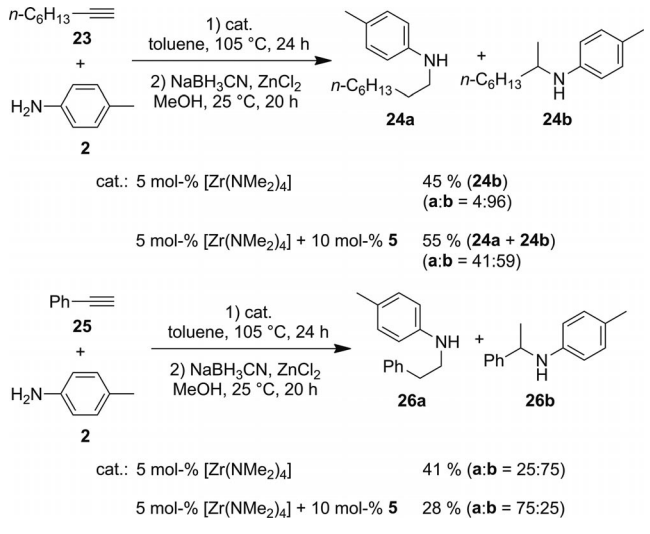
Table 4. Hydroamination/reduction sequence performed in the presence of various *N*-(*t*-butyl)sulfonamides.



Entry	Sulfonamide	Yield [%][a,b]
1	 **5**	87
2	 **20**	55
3	 **21**	90
4	 **22**	82

[a] Reaction conditions: 1) Alkyne **14** (2.0 mmol), amine **2** (2.2 mmol), $[Zr(NMe_2)_4]$ (0.1 mmol, 5 mol-%), sulfonamide (0.2 mmol, 10 mol-%), toluene (2 mL), 160 °C, 96 h; 2) $NaBH_3CN$ (4.0 mmol), $ZnCl_2$ (2.0 mmol), MeOH (10 mL), 25 °C, 20 h. [b] Yields refer to isolated pure compounds.

1-octyne (**23**) and *p*-toluidine (**2**) with the catalyst precursor $[Zr(NMe_2)_4]$ whereas the regioselectivity was only 41:59 when the reaction was performed in the presence of 10 mol-% of the additive **5**. In this context it must be noted that the observed preference for the formation of the Markovnikov regioisomer **24b** is in good agreement with the corresponding results reported for the Ti-catalyzed addition of arylamines to terminal alkylalkynes.[1b,1c,15,16] An even stronger effect was found for the addition of *p*-toluidine (**2**) to phenylacetylene (**25**). Although use of the catalyst $[Zr(NMe_2)_4]$ led to the preferred formation of the Markovnikov regioisomer **26b** (**26a**/**26b** = 25:75), the selectivity was reversed when a mixture of 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% sulfonamide **5** was used as the catalytic system.



Scheme 2. Hydroamination/reduction sequences with terminal alkynes using sulfonamide **5** as an additive.

Finally, we attempted additional reaction sequences with the secondary amines morpholine and *N*-methylbenzylamine. However, by using a mixture of 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% sulfonamide **5** as the catalyst system, no reaction was observed with the alkynes 1-phenylpropyne (**1**) and phenylacetylene (**25**) when the hydroamination step was performed at 105 or 130 °C for 96 h.

Conclusions

We have shown that zirconium-based catalyst systems can be used successfully for intermolecular hydroamination reactions of alkynes with primary amines that are sterically less demanding than 2,6-dimethylaniline. The catalysts can be simply generated in situ by using a combination of 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% of a sulfonamide in toluene and stirring the mixture at room temperature for 2 h prior to the addition of the substrates. At elevated temperatures, hydroamination can be achieved with internal and terminal alkynes as well as with sterically demanding and less demanding primary amines. In contrast, secondary amines do not react under identical conditions. Of the sulfonamide additives investigated in our study, sterically demanding tosylamides such as *N*-(*tert*-butyl)-*p*-toluenesulfonamide (**5**) gave the best results. Interestingly, the regioselectivity of the addition of amines to unsymmetrically substituted internal as well as terminal alkynes is significantly influenced by the nature of the sulfonamide additive. In particular, the successful use of sterically less demanding primary amines such as *n*-hexyl- or benzylamine clearly indicates that the simple assumption that Zr catalysts irreversibly form catalytically inactive bridging μ^2-imido dimers or other unreactive intermediates in the presence of these amines[1c] is not correct. This finding is very important for a better and more general understanding of the mechanism of group 4 metal-catalyzed hydroamination reactions.

Experimental Section

General: All reactions were performed under an inert atmosphere of nitrogen in oven-dried Schlenk tubes (Duran glassware, 100 mL, Ø 30 mm) equipped with Teflon® stopcocks and magnetic stirring bars (15 × 4.5 mm). $[Zr(NMe_2)_4]$, *N*-methyl-*p*-toluenesulfonamide (**4**), and toluene (extra dry toluene with molecular sieves) were purchased from Acros Organics. Prior to use, volatile alkynes and amines were purified and dried by distillation (20 cm Vigreux column) from CaH_2 on molecular sieves at ambient pressure under an inert atmosphere. Diphenylacetylene (**14**) was purified by kugelrohr distillation. The synthesis and purification of the sulfonamides **5**–**9** and **20**–**22** are described in the Supporting Information. All other reagents were purchased from commercial sources and were used without further purification. All alkynes, amines, sulfonamides, and

$[Zr(NMe_2)_4]$ were stored in a nitrogen-filled glove-box (M. Braun, Unilab). Unless otherwise noted, yields refer to isolated yields of pure compounds as gauged by thin-layer chromatography (TLC) and ^1H and ^{13}C NMR spectroscopy. The ratio of regioisomers was determined by gas chromatography prior to purification by flash chromatography. For TLC, Polygram® SIL G/UV254 plates from Macherey–Nagel were used. The substances were detected with UV light and/or iodine. For flash chromatography, silica gel from Fluka (particle size 0.040–0.063 mm) was used. Prior to use in flash chromatography, light petroleum ether (PE, boiling range 40–60 °C) and EtOAc were distilled. All products were identified by comparison of their ^1H and ^{13}C NMR spectroscopic data with those reported in the literature.[15,17] NMR spectra were recorded with Bruker Avance DRX 500 and Bruker Avance III 500 MHz spectrometers. All NMR spectra are reported in δ (ppm) relative to the signal of TMS at δ = 0.00 ppm (^1H NMR) and to the central line of the triplet of $CDCl_3$ at δ = 77.0 ppm (^{13}C NMR). GC analyses were performed with a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector.

General Procedure for the Hydroamination of Alkynes: A Schlenk tube equipped with a Teflon® stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glove-box and charged with $[Zr(NMe_2)_4]$ (0.1 mmol, 5 mol-%), toluene (0.3 mL), a sulfonamide (0.2 mmol, 10 mol-%) and toluene (0.7 mL). The resulting mixture was stirred for 2 h at room temperature. Then the alkyne (2.0 mmol), the amine (2.2 mmol), and toluene (1.0 mL) were added to the Schlenk tube. The tube was sealed and the resulting mixture was heated at 105–160 °C for 24–96 h. After the mixture had cooled to room temperature, $NaBH_3CN$ (302 mg, 4.80 mmol, 2.0 equiv.), $ZnCl_2$ (328 mg, 2.40 mmol, 1.0 equiv.), and MeOH (10 mL) were added. After stirring this mixture at 25 °C for 20 h, CH_2Cl_2 (50 mL) and saturated aqueous Na_2CO_3 solution (20 mL) were added. The resulting mixture was filtered and the solid residue was washed with CH_2Cl_2 (50 mL). After extraction, the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (6 × 50 mL) and the combined organic layers were dried with $MgSO_4$. After concentration under vacuum, the regioisomeric ratio was determined by GC (if applicable), and the crude product was purified by flash chromatography (SiO_2).

Amines 3a and 3b:[15] The general procedure was used to synthesize a mixture of **3a** and **3b** from 1-phenylpropyne (**1**; 232 mg, 2.0 mmol) and *p*-toluidine (**2**; 235 mg, 2.2 mmol). The hydroamination was performed at 130 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). The regioisomeric ratio **3a/3b** was determined to be 86:14. After purification by flash chromatography (PE/EtOAc, 20:1), a mixture of **3a** and **3b** (335 mg, 1.49 mmol, 74%) was obtained as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, mixture of **3a** and **3b**): δ = 1.18 (t, *J* = 7.4 Hz, 3 H), 1.36 (d, *J* = 6.5 Hz, 3 H), 1.95–2.20 (m, 2 H), 2.43 (s, 3 H), 2.51 (s, 3 H), 2.90 (dd, *J* = 7.4, 13.4 Hz, 1 H), 3.16 (dd, *J* = 4.7, 13.4 Hz, 1 H), 3.60 (br. s, 1 H), 3.90–4.05 (m, 1 H), 4.43 (t, *J* = 6.7 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.3 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.30–7.65 (m, 2× 5 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, mixture of **3a** and **3b**): δ = 10.7 (CH_3), 20.0 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 31.5 (CH_2), 42.1 (CH_2), 49.5 (CH), 59.8 (CH), 113.2 (CH), 113.5 (CH), 126.1 (CH), 126.2 (CH), 128.2 (CH), 129.4 (CH), 129.5 (CH), 129.8 (CH), 138.5 (C), 144.0 (C), 144.8 (C), 145.1 (C) ppm.

Amines 12a and 12b:[15] The general procedure was used to synthesize a mixture of **12a** and **12b** from 1-phenylpropyne (**1**; 232 mg, 2.0 mmol) and cyclopentylamine (**10**; 173 mg, 2.2 mmol). The hydroamination was performed at 130 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). The regioisomeric ratio **12a/12b** was determined to be 53:47. After purification by flash chromatography (PE/EtOAc, 40:1), a mixture of **12a** and **12b** (267 mg, 1.30 mmol, 65%) was obtained as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, important signals of the mixture of **12a** and **12b**): δ = 0.71 (t, *J* = 7.4 Hz, 3 H), 0.98 (d, *J* = 6.2 Hz, 3 H), 2.51 (dd, *J* = 6.2 Hz, 3 H), 2.67 (dd, *J* = 6.2 Hz, 3 H), 2.78 (quint., *J* = 7.1 Hz, 1 H), 2.89 (sext, *J* = 6.4 Hz, 1 H), 3.11 (quint., *J* = 7.1 Hz, 1 H), 3.45 (dd, *J* = 5.9, 8.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, important signals of the mixture of **12a** and **12b**): δ = 10.9 (CH_3), 20.5 (CH_3), 52.9 (CH), 56.9 (CH), 57.1 (CH), 63.5 (CH), 139.6 (C), 144.5 (C) ppm.

Amines 13a and 13b:[17] The general procedure was used to synthesize a mixture of **13a** and **13b** from 1-phenylpropyne (**1**; 232 mg, 2.0 mmol) and *n*-hexylamine (**11**; 206 mg, 2.2 mmol). The hydroamination was performed at 130 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). The regioisomeric ratio **13a/13b** was determined to be 50:50. After purification by flash chromatography (PE/EtOAc, 40:1), a mixture of **13a** and **13b** (202 mg, 0.92 mmol, 46%) was obtained as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, important signals of the mixture of **13a** and **13b**): δ = 0.70 (t, *J* = 7.5 Hz, 3 H), 0.96 (d, *J* = 6.3 Hz, 3 H), 2.79 (sext, *J* = 6.4 Hz, 1 H), 3.37 (dd, *J* = 5.8, 8.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, important signals of the mixture of **13a** and **13b**): δ = 10.6 (CH_3), 13.8 (CH_3), 14.0 (CH_3), 20.0 (CH_3), 21.2 (CH_3), 43.4 (CH_2), 47.2 (CH_2), 47.6 (CH_2), 54.5 (CH), 65.0 (CH), 139.3 (C), 144.1 (C) ppm.

Amine 16:[15] The general procedure was used to synthesize **16** from diphenylacetylene (**14**; 356 mg, 2.0 mmol) and *p*-toluidine (**2**; 235 mg, 2.2 mmol). The hydroamination was performed at 160 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). After purification by flash chromatography (PE/EtOAc, 40:1), product **16** (499 mg, 1.74 mmol, 87%) was obtained as a beige solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 2.91 (dd, *J* = 8.2, 14.0 Hz, 1 H), 3.03 (dd, *J* = 5.7, 14.0 Hz, 1 H), 3.89 (br. s, 1 H), 4.47 (dd, *J* = 5.7, 8.2 Hz, 1 H), 6.29 (d, *J* = 8.5 Hz, 2 H), 6.77 (d, *J* = 8.1 Hz, 2 H), 7.09–7.29 (m, 10 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 20.3 (CH_3), 45.1 (CH_2), 59.4 (CH), 113.8 (CH), 126.5 (CH), 126.5 (C), 126.6 (CH), 128.5 (CH), 128.5 (CH), 129.2 (CH), 129.5 (CH), 131.6 (CH), 137.8 (C), 143.6 (C), 145.0 (C) ppm.

Amine 17:[15] The general procedure was used to synthesize **17** from diphenylacetylene (**14**; 356 mg, 2.0 mmol) and cyclopentylamine (**10**; 173 mg, 2.2 mmol). The hydroamination was performed at 160 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). After purification by flash chromatography (PE/EtOAc, 40:1), product **17** (368 mg, 1.39 mmol, 70%) was obtained as a beige solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95–1.08 (m, 2 H), 1.18–1.28 (m, 2 H), 1.30–1.44 (m, 2 H), 1.51–1.64 (m, 2 H), 2.69–2.85 (m, 3 H), 3.80 (dd, *J* = 6.1, 8.1 Hz, 1 H), 6.94–7.24 (m, 10 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 23.3 (CH_2), 23.3 (CH_2), 32.1 (CH_2), 33.5 (CH_2), 45.2 (CH_2), 57.1 (CH), 63.0 (CH), 126.0 (CH), 126.7 (CH), 127.1 (CH), 128.0 (CH), 128.1 (CH), 129.0 (CH), 138.8 (C), 144.0 (C) ppm.

Amine 18:[15] The general procedure was used to synthesize **18** from diphenylacetylene (**14**; 356 mg, 2.0 mmol) and *n*-hexylamine (**11**; 206 mg, 2.2 mmol). The hydroamination was performed at 160 °C for 96 h with 5 mol-% $[Zr(NMe_2)_4]$ and 10 mol-% *t*BuNH*p*Ts (**5**). After purification by flash chromatography (PE/EtOAc, 40:1), product **18** (523 mg, 1.86 mmol, 93%) was obtained as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.2 Hz, 3 H), 1.22–1.36 (m, 6 H), 1.38–1.50 (m, 2 H), 1.54 (br. s, 1 H), 2.41–2.55

(m, 2 H), 2.98 (dd, J = 8.3, 13.4 Hz, 1 H), 3.04 (dd, J = 5.9, 13.4 Hz, 1 H), 3.94 (dd, J = 5.9, 8.2 Hz, 1 H), 7.20–7.45 (m, 10 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 13.7 (CH_3), 22.3 (CH_2), 26.5 (CH_2), 29.6 (CH_2), 31.4 (CH_2), 45.1 (CH_2), 47.4 (CH_2), 64.6 (CH), 126.0 (CH), 126.6 (CH), 127.0 (CH), 127.9 (CH), 128.0 (CH), 128.9 (CH), 138.7 (C), 143.8 (C) ppm.

Amine 19:[15] The general procedure was used to synthesize **19** from diphenylacetylene (**14**; 356 mg, 2.0 mmol) and benzylamine (**15**; 235 mg, 2.2 mmol). The hydroamination was performed at 160 °C for 96 h with 5 mol-% [$Zr(NMe_2)_4$] and 10 mol-% *t*BuNH*p*Ts (**5**). After purification by flash chromatography (PE/EtOAc, 20:1), product **19** (391 mg, 1.36 mmol, 68%) was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.82 (br. s, 1 H), 2.92–3.11 (m, 2 H), 3.55 (d, J = 13.6 Hz, 1 H), 3.75 (d, J = 13.6 Hz, 1 H), 3.98 (dd, J = 5.5, 8.5 Hz, 1 H), 7.15–7.22 (m, 4 H), 7.25–7.50 (m, 11 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 45.3 (CH_2), 51.3 (CH_2), 63.6 (CH), 126.3 (CH), 126.7 (CH), 127.1 (CH), 127.4 (CH), 127.9 (CH), 128.2 (CH), 128.3 (CH), 129.2 (CH), 138.8 (C), 140.4 (C), 143.7 (C) ppm.

Amine 24b:[15] The general procedure was used to synthesize **24b** from 1-octyne (**23**; 220 mg, 2.0 mmol) and *p*-toluidine (**2**; 235 mg, 2.2 mmol). The hydroamination was performed at 105 °C for 24 h with 5 mol-% [$Zr(NMe_2)_4$]. The regioisomeric ratio **24a**/**24b** was determined to be 4:96. After purification by flash chromatography (PE/EtOAc, 20:1), **24b** (197 mg, 0.90 mmol, 45%) was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, J = 6.4 Hz, 3 H), 1.06 (d, J = 6.4 Hz, 3 H), 1.15–1.42 (m, 9 H), 1.44–1.52 (m, 1 H), 2.14 (s, 3 H), 3.29–3.33 (m, 2 H), 6.44 (d, J = 8.2 Hz, 2 H), 6.88 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 14.0 (CH_3), 20.3 (CH_3), 20.7 (CH_3), 22.6 (CH_2), 26.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 37.1 (CH_2), 48.9 (CH), 113.4 (CH), 126.0 (C), 129.7 (CH), 145.2 (C) ppm.

Amines 26a and 26b:[15] The general procedure was used to synthesize a mixture of **26a** and **26b** from phenylacetylene (**25**; 204 mg, 2.0 mmol) and *p*-toluidine (**2**; 235 mg, 2.2 mmol). The hydroamination was performed at 105 °C for 24 h with 5 mol-% [$Zr(NMe_2)_4$] and 10 mol-% *t*BuNH*p*Ts (**5**). The regioisomeric ratio **26a**/**26b** was determined to be 75:25. After purification by flash chromatography (PE/EtOAc, 20:1), a mixture of **26a** and **26b** (115 mg, 0.56 mmol, 28%) was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, mixture of **26a** and **26b**): δ = 1.42 (d, J = 6.7 Hz, 3 H), 2.11 (s, 3 H), 2.16 (s, 3 H), 2.83 (t, J = 7.0 Hz, 2 H), 3.30 (t, J = 7.0 Hz, 3 H), 3.66 (br. s, 1 H), 4.37 (q, J = 6.7 Hz, 1 H), 6.35 (d, J = 8.2 Hz, 2 H), 6.47 (d, J = 8.2 Hz, 2 H), 6.82 (d, J = 8.2 Hz, 2 H), 6.92 (d, J = 8.1 Hz, 2 H), 7.14–7.28 (m, 2× 5 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, mixture of **a** and **b**): δ = 20.3 (CH_3), 20.4 (CH_3), 25.0 (CH_3), 35.5 (CH_2), 45.4 (CH_2), 53.6 (CH), 113.2 (CH), 113.4 (CH), 125.8 (CH), 126.4 (CH), 126.7 (C), 126.8 (CH), 128.6 (CH), 128.8 (CH), 129.6 (CH), 129.8 (CH), 139.4 (C), 145.0 (C), 145.4 (C), 145.7 (C) ppm.

Supporting Information (see footnote on the first page of this article): Experimental details for the synthesis of sulfonamides and characterization data.

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