Zirconium-Catalyzed Intermolecular Hydroamination of Unactivated Olefins

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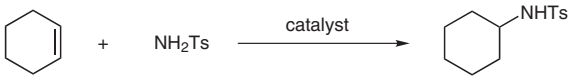
Abstract: Highly efficient hydroamination reactions of sulfonamides, carboxamides, and carbamates with unactivated olefins catalyzed by simple and inexpensive zirconium salts under mild reaction conditions were presented for the practical preparation of various amines. These processes gave good to excellent yields of the addition products in Markovnikov addition fashion.

Key words: hydroamination, olefins, amides, carbamates, zirconium salts

Hydroamination, the simple addition of an N–H bond across an C–C unsaturated organic fragment, has attracted much attention in the past decades.[1,2] This synthetic transformation is highly efficient due to the highly atom-economic synthesis and the readily availability of the starting materials. Further exploration of the hydroamination of unactivated alkenes continues to be an important area of research.[3–5] Some time ago Marks and coworkers demonstrated that lanthanide-based catalysts could be used in hydroamination of a broad substrate scope in both the olefin and the amines.[6] Recently, efficient platinum(II),[7] gold(I),[8] copper(II),[9] and other metal salts[10] were reported to catalyze the hydroamination of amides and carbamates. Along with the metal catalysts, there were also examples using metal-free catalysts for the hydroamination of olefins and amides.[11] Although some notable progress have been made on the hydroamination reactions of alkenes with amides in the past two years, there were also drawbacks on the reported methods, such as using expensive and toxic metals, higher temperature, and tedious reaction procedures. Therefore, the development of a general, efficient, and readily available or practical catalyst for hydroamination reactions of unactivated alkenes with sulfonamides, carboxamides, and carbamates is highly desirable.

In the past decades, significant progress has been achieved through the use of group IV metal complexes for hydroamination reactions of alkynes and allenes.[12] However, catalysts using the simple group IV metal salts were limited in this reaction.[13] To the best of our knowledge, no example of zirconium-catalyzed intermolecular alkene hydroamination with weaker nucleophiles such as sulfonamides, carboxamides, and carbamates have been reported.[14] Herein we wish to report our recent findings that $Zr(OTf)_4$ could be used to catalyze the hydroamination between unactivated olefins and sulfonamides, carbamates, or amides under mild reaction conditions.

Table 1 Catalyst and Solvent Screening for Hydroamination between *p*-Toluenesulfonamide and Cyclohexene[a]



Entry	Catalyst (loading, mol%)	Time (h)	Solvent	Yield (%)[b]
1	$Cu(OTf)_2$ (5)	22	toluene	trace
2	$Sm(OTf)_3$ (10)	22	toluene	0
3	$Ni(OTf)_2$ (10)	22	toluene	0
4	$Zn(OTf)_2$ (10)	22	toluene	0
5	$Zr(OTf)_4$ (5)	22	toluene	94
6	$ZrOCl_2 \cdot 8H_2O$ (5)	22	toluene	trace
7	$Zr(SO_4)_2 \cdot 4H_2O$ (5)	22	toluene	trace
8	$ZrCl_4$ (5)	22	toluene	<10
9[c]	$Zr(OTf)_4$ (5)	24	toluene	<10
10	$Zr(OTf)_4$ (5)	20	DCE	95
11	$Zr(OTf)_4$ (5)	20	1,4-dioxane	38
12	$Zr(OTf)_4$ (5)	20	*n*-heptane	97
13	$Zr(OTf)_4$ (2.5)	20	*n*-heptane	96

[a] Reactions were conducted in solvent (2 mL) with cyclohexene (2 mmol) and NH_2Ts (1 mmol) in the presence of different catalyst at 85 °C.
[b] Determined by GC analysis with internal standard.
[c] The reaction was carried out at r.t.

In preliminary experiments, hydroamination of cyclohexene with *p*-toluenesulfonamide was carried out in the presence of several readily available Lewis acids in toluene at 85 °C (Table 1).[15] Zirconium triflate[16] gave the highest yield of *N*-cyclohexyl *p*-toluenesulfonamide (Table 1, entry 5). Other Lewis acids, such as $Zn(OTf)_2$, $Sm(OTf)_3$, $Ni(OTf)_2$ could not catalyze the same reaction at all even at higher catalyst loading (10 mol%). To vali-

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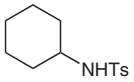
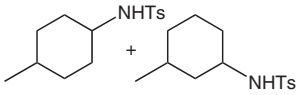
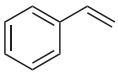
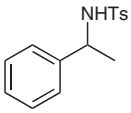
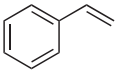
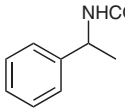
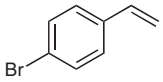
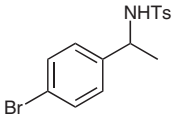
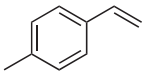
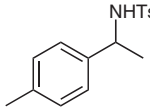
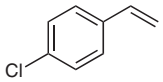
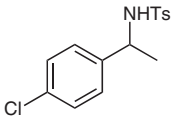
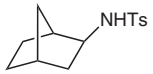
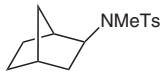
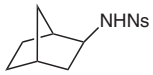
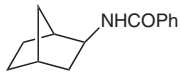
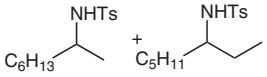
date the unique reactivity of the catalyst, several control experiments were conducted in the presence of other zirconium salts. For example, $ZrSO_4$, $ZrCl_4$, and $ZrOCl_2$ did not catalyze the hydroamination reaction (entries 6–8). These results indicated that the combination of the triflate counteranion and the zirconium cation were all very important for achieving higher product yield. A series of solvents was screened (entries 9–12). We found that

Table 2 Hydroamination of Unactivated Olefins with Amides[a]

Entry	Olefin	Amide	Time (h)	Temp (°C)	Product	Yield (%)[b]
1		$TsNH_2$	20	85		93[c]
2		$TsNH_2$	24	85		80[c]
3[d]		$TsNH_2$	24	85		64 (1:1)
4[d]		$TsNH_2$	20	45		90
5[e]		$PhCONH_2$	25	100		60
6[d]		$TsNH_2$	20	45		93
7[d]		$TsNH_2$	20	r.t.		68
8[e]		$TsNH_2$	30	85		75
9[f]		$TsNH_2$	24	85		95
10[f]		$TsNHCH_3$	24	85		82
11[e]		*p*-$NsNH_2$	20	85		72
12[e]		$PhCONH_2$	24	100		25[g]
13[f]		$TsNH_2$	40	90		68 (2:1)[h]

[a] Reactions were conducted with nucleophiles (1 mmol), olefins (2 mmol), and $Zr(OTf)_4$ (5 mol%) in *n*-heptane (2 mL).
[b] Isolated yield.
[c] Amount of $Zr(OTf)_4$ used = 2.5 mol%.
[d] Toluene was used as solvent.
[e] 1,4-Dioxane as solvent.
[f] DCE was used as solvent.
[g] Amount of $Zr(OTf)_4$ used = 10 mol%.
[h] Amount of olefin used = 3 mmol.

coordinating solvents such as 1,4-dioxane tended to shut down the reaction, whereas noncoordinating solvents such as 1,2-dichloroethane (DCE), *n*-heptane, and toluene seemed to be ideal. Consequently, good yield was obtained even when using 1 mol% of $Zr(OTf)_4$ as the catalyst (76% of isolated yield).

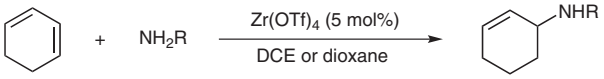
With the above optimized reaction conditions in hand, hydroamination of various nitrogen nucleophiles and different olefins were also investigated. The results are summarized in Table 2.

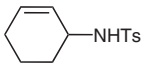
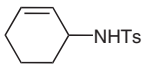
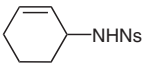
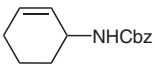
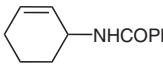
Cyclic unactivated alkenes, such as cycloheptene and cyclohexene, were found to be good acceptors with NH_2Ts (entries 1–3). When using styrene as the olefin (entry 4), high yield of the addition product was obtained in toluene under mild reaction conditions (45 °C). The addition of benzamide to styrene also occurred under modified conditions (entry 5). The reactions of $TsNH_2$ with 4-bromostyrene produced a fast and high-yielding reaction (entry 6), while the reaction of 4-chlorostyrene was somewhat slower (entry 8). Interestingly, in the presence of electron-donating groups such as 4-Me, the reactions could be carried out at room temperature in good yield (entry 7). Additions of amide to the more strained norbornene were also studied (entries 9–12). For example, best yields were obtained with NH_2Ts or $TsNHCH_3$, and moderate yield with the less nucleophilic 4-nitrobenzenesulfonamide (*p*-$NsNH_2$). It should be noted that the reaction of benzamide and norbornene was very sluggish, affording product in 25% yield after 24 hours using 10 mol% $Zr(OTf)_4$ as the catalyst. The reaction between $TsNH_2$ and an excess (3 equiv) of 1-octene occurred in moderate yield to form an approximately 2:1 ratio of the 2- and 3-*N*-octyl tosylamides (entry 13).

Next, we further extended the scope of this methodology by subjecting various amides as nucleophiles for the hydroamination of 1,3-cyclohexadiene.[17] As shown in Table 3, the catalytic hydroamination of NH_2Ts with 1,3-cyclohexadiene in the presence of 5% $Zr(OTf)_4$ was nearly completed after 10 hours at 50 °C to form the addition product in 86% isolated yield (Table 3, entry 1). Remarkably, this addition reaction could proceed smoothly at room temperature. This demonstrated the unique catalytic activity of $Zr(OTf)_4$ as compared to $Cu(OTf)_2$, which was ineffective alone in the hydroamination of NH_2Ts with 1,3-cyclohexadiene.[9] It was interesting to find that *p*-$NsNH_2$ was not a suitable candidate for this reaction (entry 3). Zirconium triflate was also applied to hydroamination of NH_2Cbz with 1,3-cyclohexadiene to give products in good yield (entry 4). On the other hand, lower reactive $PhCONH_2$ and 1,3-cyclohexadiene only gave moderate results even at relatively higher temperature (entry 5).

In summary, we presented herein that $Zr(OTf)_4$ could efficiently catalyze the addition of sulfonamides, carboxamides, and carbamates to various unactivated olefins. The wide substrate scope, relatively inexpensive catalyst, simple operation, and lower ratio of olefin to nitrogen source are the advantages of this process. Although the exact mechanism was not clear at this current stage, on the basis of the results obtained from the group IV metal complex catalyzed hydroamination reactions,[12,13] the generation of zirconium–imido complexes was probably involved in our present reaction. Further explorations of this work to asymmetric hydroamination and other heterofunctionalization of olefin or alkynes are undergoing in our groups.

Table 3 $Zr(OTf)_4$-Catalyzed Hydroamination of 1,3-Cyclohexadiene with Amines



Entry[a]	Amine	Temp (°C)	Time (h)	Product	Yield (%)[b]
1	$TsNH_2$	50	10		86
2	$TsNH_2$	r.t.	10		48
3[c]	*p*-$NsNH_2$	90	21		<10
4	NH_2Cbz	50	22		74
5[d]	$PhCONH_2$	100	24		55

[a] Reactions were conducted with nucleophiles (1 mmol), 1,3-cyclohexadiene (1.2 mmol), and $Zr(OTf)_4$ (5 mol%) in DCE (2 mL).
[b] Isolated yield.
[c] 1,4-Dioxane was used as solvent.
[d] The amount of 10 mol% of $Zr(OTf)_4$ was used.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(14) During the preparation of our manuscript, several related papers using other metal salts dealing with the intermolecular hydroamination of styrenes have appeared in the literature, see ref. 10a–c.

(15) **Typical Procedure for Intermolecular Addition Reactions of Olefins**

Into a test tube were placed $Zr(OTf)_4$ (0.05 mmol) and NH_2Ts (1 mmol). After the test tube was sealed, it was purged three times with argon, then *n*-heptane (2 mL) and cyclohexene (2 mmol) were injected. The reaction mixture was heated at 85 °C and stirred vigorously for 20 h. After the reaction was completed, the mixture was directly applied to column chromatography using SiO_2 (EtOAc–PE, 1:10 to 1:5) to afford a analytically pure product (93% isolated yield). All the compounds are known and NMR or GC-MS data for some representative products are given below.

***N*-(1-Phenylethyl)benzamide**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.2 Hz, 2 H), 7.50–7.46 (t, 1 H), 7.42–7.35 (m, 6 H), 7.33–7.25 (m, 1 H), 6.44 (br, 1 H), 5.34 (dt, *J* = 7.2, 7.2 Hz, 1 H), 1.60 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.56, 143.08, 134.51, 131.42, 128.70, 128.50, 127.40, 126.89, 126.21, 49.17, 21.68. GC-MS: *m/z* = 225.

***N*-[1-(4-Bromophenyl)ethyl]-4-methylbenzenesulfonamide**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H,), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 5.42 (d, *J* = 7.2 Hz, 1 H), 4.41 (quint, *J* = 6.8 Hz, 1 H), 2.39 (s, 3 H), 1.37 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.32, 140.00, 137.33, 131.43, 129.42, 127.92, 127.00, 121.16, 53.06, 23.35, 21.47. GC-MS: *m/z* = 354.

Cyclohex-2-enyl-*p*-toluenesulfonamide

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 5.71 (d, *J* = 10.0 Hz, 1 H), 5.31 (d,

J = 10.4 Hz, 1 H), 4.84 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 1 H), 2.39 (s, 3 H), 1.94–1.77 (m, 2 H), 1.74–1.61 (m,1 H), 1.57–1.50 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.14, 138.24, 131.39, 129.60, 126.95, 126.91, 48.89, 30.12, 24.38, 21.45, 19.22. GC-MS: *m/z* = 251.

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