FULL PAPERS

Bismuth- and Hafnium-Catalyzed Hydroamination of Vinyl Arenes with Sulfonamides, Carbamates, and Carboxamides

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Abstract: Catalytic intermolecular hydroamination of vinyl arenes is described. Our initial investigation revealed that a Bi(OTf)$_3$/[Cu-(CH$_3$CN)$_4$]PF$_6$ system previously developed for catalytic intermolecular hydroamination of 1,3-dienes was suitable for hydroamination of a styrene with sulfonamides, but the substrate generality of this system was unsatisfactory. Several metals were screened to expand the substrate scope, and a new Hf(OTf)$_4$/[Cu(CH$_3$CN)$_4$]PF$_6$ system was determined to be highly suitable. The combination of Hf(OTf)$_4$ and [Cu-(CH$_3$CN)$_4$]PF$_6$ efficiently promoted the hydroamination of various vinyl arenes, including less-reactive vinyl arenes with electron-withdrawing groups. This strategy was applied to sulfonamides, carbamates, and carboxamides, and products were obtained in up to 99 % yield with 0.3–10 mol % catalyst loading.

Keywords: bismuth · hafnium · homogeneous catalysis · hydroamination · synthetic methods

Introduction

The importance of amine derivatives for the synthesis of pharmaceuticals and fine chemicals has attracted considerable interest in catalytic olefin amination.[1] Intermolecular hydroamination of olefins is one of the most important topics in this area. Tremendous progress was recently achieved in intermolecular hydroamination with alkylamines and arylamines using transition-metal complexes, lanthanide metallocenes, and other systems.[2,3,4] There remains room for improvement, however, in intermolecular hydroamination with electron-deficient amine nucleophiles such as sulfonamides, carbamates, and carboxamides.[5,6] Recently, efficient Pt^{II}-[5a,b] and Au^{I}-catalyzed[5c,d,e] intermolecular hydroaminations of unactivated olefins, vinyl arenes, and 1,3-dienes with amides were reported.[7] In the reaction of vinyl arenes, however, either high reaction temperature (85–120 °C) or microwave irradiation was required with Pt^{II}[5a] and Au^{I} catalysts.[5c,d] Furthermore, the use of vinyl arenes with electron-withdrawing groups was quite limited, probably owing to their attenuated reactivity. Recently, efficient Cu-catalyzed intermolecular hydroamination of various vinyl arenes, including those with electron-withdrawing groups, was reported.[8] Products were obtained in excellent yield, although only two sulfonamides, toluenesulfonyl (Ts) and nitrobenzenesulfonyl (Ns), were utilized at relatively high temperature (75 °C). This work prompted us to report our approach towards this task. Herein, we describe bismuth- and hafnium-catalyzed[9] intermolecular hydroamination of vinyl arenes with sulfonamides, carbamates, and carboxamides. The present catalysts are especially suitable for vinyl arenes with electron-withdrawing groups.

Results and Discussion

We recently reported a bismuth-catalyzed intermolecular hydroamination of 1,3-dienes with sulfonamides, carbamates, and carboxamides.[10,11] In the reaction, the combination of Bi(OTf)$_3$ (Tf = trifluoromethanesulfonyl) with MPF$_6$ (M = K or [Cu(CH$_3$CN)$_4$]) was essential to achieve a high yield. Mechanistic studies suggested that the active species is cationic Bi(OTf)$_2$·PF$_6$, which functions as a π acid to activate 1,3-dienes to generate a carbenium intermediate. Therefore, we initially tried to apply the bismuth catalyst to the hydroamination of vinyl arenes. The optimization of the reaction conditions is summarized in Table 1. Bi(OTf)$_3$/KPF$_6$ (**4a**) promoted the reaction of styrene **1a** (1.2 equiv) and sulfonamide **2a** at 25 °C (Table 1, entry 1; 54 % yield). The additive

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Table 1. Optimization of reaction conditions.

Entry	Bi(OTf)$_3$ [mol%]	Additive	[mol%]	1a [equiv]	T [°C]	Yield[a] [%]
1	10	KPF$_6$ (4a)	10	1.2	25	54
2	10	[Cu(CH$_3$CN)$_4$]PF$_6$ (4b)	10	1.2	25	62
3	10	none	0	1.2	25	21
4	0	4b	10	1.2	25	0
5	10	NH$_4$PF$_6$ (4c)	10	1.2	25	44
6	10	4b	10	2.0	25	78
7	10	4b	10	2.0	40	91

[a] Yield of isolated analytically pure compounds after purification by column chromatography.

[Cu(CH$_3$CN)$_4$]PF$_6$ (4b) gave slightly better results (Table 1, entry 2; 62% yield). The results of a control experiment with either Bi(OTf)$_3$ (Table 1, entry 3) or 4b (Table 1, entry 4) alone at 25°C were not satisfactory. On the other hand, the addition of NH$_4$PF$_6$ (4c) slightly improved the reactivity (Table 1, entry 5; 44% yield). The results in Table 1, entries 1–5 suggest that both bismuth and PF$_6^-$ are important for achieving good reactivity at 25°C. By increasing the amount of 1a (2 equiv), the yield of 3aa increased to 78% (Table 1, entry 6). At 40°C, 3aa was obtained in 91% yield (Table 1, entry 7).

Bi(OTf)$_3$/4b was applied to hydroaminations of styrene 1a with sulfonamides 2a–2f to give products in good yield (Table 2, entries 1–6; 80–97% yield). With p-TsNH$_2$ (2b), the reaction proceeded smoothly at 25°C (Table 2, entry 2; 87% yield). On the other hand, sulfonamide 2g and carbamate 2h gave less-satisfactory results (Table 2, entries 7 and 8; 54% and 33% yield, respectively). The generality of vinyl arenes was also narrow with the Bi(OTf)$_3$/4b system, as shown in Table 2, entries 9 and 10.

To expand the substrate scope of the reaction, we reinvestigated metal sources with vinyl arene 1a and carbamate 2h (Table 3). Among the metals examined, Hf(OTf)$_4$ gave

Abstract in Japanese:

我々は既にビスマス触媒を用い、アミドを求核剤とする1,3‐ジエンの触媒的分子間ヒドロアミノ化反応について報告している。今回、ビニルアレーン類に対するアミドを求核剤とする触媒的分子間ヒドロアミノ化反応について検討を行った。1,3‐ジエンに対して有効であったBi(OTf)$_3$/Cu(CH$_3$CN)$_4$PF$_6$触媒系はスルホンアミドとスチレンとの反応に対しても有効ではあったものの、基質一般性に問題があることがわかった。より優れた触媒系の探索を行った結果、新たにHf(OTf)$_4$/Cu(CH$_3$CN)$_4$PF$_6$触媒系が反応性の低い電子求引性の置換基をもつビニルアレーン類を含む幅広い基質へ適用可能であることを見いだした。0.3‐10 mol%の触媒量存在下、各種アミド求核剤を用いた分子間ヒドロアミノ化反応が進行し、最高99%収率で生成物を与えた。

Table 2. Bismuth-catalyzed hydroamination of vinyl arenes.

Entry	1 X		2		Product	T [°C]	Yield[a] [%]
1	H	1a	PhSO$_2$-NH$_2$	2a	3aa	40	91
2	H	1a	p-Ts-NH$_2$	2b	3ab	25	87
3	H	1a	o-Ts-NH$_2$	2c	3ac	40	90
4	H	1a	p-MeO-C$_6$H$_4$SO$_2$-NH$_2$	2d	3ad	40	97
5	H	1a	p-CF$_3$-C$_6$H$_4$SO$_2$-NH$_2$	2e	3ae	40	80
6	H	1a	p-Cl-C$_6$H$_4$SO2-NH$_2$	2f	3af	40	88
7	H	1a	o-Ns-NH$_2$	2g	3ag	40	54
8	H	1a	[structure]	2h	3ah	40	33
9	4-Cl	1b	p-Ts-NH$_2$	2b	3bb	40	59
10	4-Me	1c	p-Ts-NH$_2$	2b	3cb	25	trace

[a] Yield of isolated analytically pure compounds after purification by column chromatography.

Table 3. Metal effects in hydroamination of vinyl arene 1a with carbamate 2h.

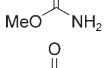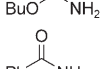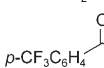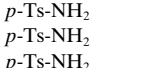| Entry	Metal	T [°C]	Yield[a] [%]	Entry	Metal	T [°C]	Yield[a] [%]
1	Bi(OTf)$_3$	40	33	5	Yb(OTf)$_3$	40	41
2	In(OTf)$_3$	40	trace	6	Cu(OTf)$_2$	40	trace
3	Sc(OTf)$_3$	40	48	7	Hf(OTf)$_4$	40	73
4	Dy(OTf)$_3$	40	48	8	Hf(OTf)$_4$	60	79
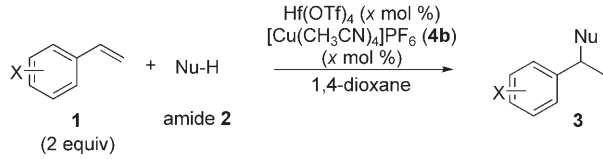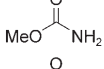
[a] Yield of isolated analytically pure compounds after purification by column chromatography.

products in 73% yield (Table 3, entry 7), whereas Bi(OTf)$_3$ gave only 33% yield (Table 3, entry 1). We also examined several other metals, such as In(OTf)$_3$, Sc(OTf)$_3$, Dy(OTf)$_3$, Yb(OTf)$_3$, and Cu(OTf)$_2$, but again unsatisfactory results were obtained (Table 3, entries 2–6, trace to 48% yield). At 60°C with Hf(OTf)$_4$, 3ah was obtained in 79% yield after 24 h (Table 3, entry 8). The Hf(OTf)$_4$/4b system was appropriate for the hydroamination of vinyl arenes with various amides. The substrate scope of Hf(OTf)$_4$/4b is summarized in Table 4. With sulfonamides, the Hf(OTf)$_4$/4b system gave comparable results with Bi(OTf)$_3$/4b. With the hafnium catalyst, hydroamination of styrene 1a proceeded smoothly with sulfonamides 2a–2g (Table 4, entries 1–9; 67–91% yield). Catalyst loading was successfully reduced to 1 mol% without difficulty (Table 4, entry 3; 90% yield). With 0.3 mol% catalyst, a good turnover number (TON=253) was realized at 25°C, although the yield of 3ab decreased to 76% (Table 4, entry 4). Notably, various vinyl arenes with

Table 4. Hafnium-catalyzed hydroamination of vinyl arenes.[a]

Entry	1 X		2		Catalyst [mol %]	Product	T [°C]	t [h]	Yield[b] [%]
1	H	1a	PhSO₂-NH₂	2a	10	3aa	40	24	90
2	H	1a	p-Ts-NH₂	2b	10	3ab	25	24	90
3	H	1a	p-Ts-NH₂	2b	1	3ab	25	24	90
4	H	1a	p-Ts-NH₂	2b	0.3	3ab	25	40	76
5	H	1a	o-Ts-NH₂	2c	10	3ac	40	24	91
6	H	1a	p-MeO-C₆H₄SO₂NH₂	2d	10	3ad	40	24	88
7	H	1a	p-CF₃-C₆H₄SO₂-NH₂	2e	10	3ae	40	24	82
8	H	1a	p-Cl-C₆H₄SO₂-NH₂	2f	10	3af	40	24	89
9	H	1a	o-Ns-NH₂	2g	10	3ag	40	24	67
10	4-Cl	1b	p-Ts-NH₂	2b	10	3bb	40	24	99
11	4-Br	1d	p-Ts-NH₂	2b	10	3db	40	24	91
12	4-F	1e	p-Ts-NH₂	2b	10	3eb	40	24	86
13	3-Cl	1f	p-Ts-NH₂	2b	10	3fb	40	24	61
14	H	1a	(oxazolidinone)	2h	10	3ah	60	24	79
15	4-Cl	1b	(oxazolidinone)	2h	10	3bh	60	24	71
16	4-Br	1d	(oxazolidinone)	2h	10	3dh	60	24	64
17	4-F	1e	(oxazolidinone)	2h	10	3eh	60	24	81
18	4-Cl	1b	MeO-C(O)-NH₂	2i	10	3bi	60	24	76
19	4-Br	1d	MeO-C(O)-NH₂	2i	10	3di	60	24	62
20	4-Cl	1b	BuO-C(O)-NH₂	2j	10	3bj	60	24	67
21	H	1a	Ph-C(O)-NH₂	2k	10	3ak	90	24	54
22	H	1a	p-CF₃C₆H₄-C(O)-NH₂	2l	10	3al	90	24	64
23	4-Me	1c	p-Ts-NH₂	2b	10	3cb	20	24	20
24[c]	4-Me	1c	p-Ts-NH₂	2b	10	3cb	20	24	44
25[c,d]	4-Me	1c	p-Ts-NH₂	2b	10	3cb	8	72	75

[a] Reaction was performed with vinyl arenes 1 (2 equiv, 0.6 mmol) and amides 2 (0.3 mmol) in 1,4-dioxane (1.0 mL) unless otherwise noted. [b] Yield of isolated analytically pure compounds after purification by column chromatography. [c] 4 equiv of vinyl arene 1c (1.2 mmol) was used. [d] DME was used alternatively.

electron-withdrawing groups, carbamates 2h–2j, and carbox-amides 2k–2l could also be used with the hafnium catalyst. The substrate scope is complementary to that in previous reports.[5,8,12] With vinyl arenes 1b, 1d–1f and sulfonamide 2b, the desired products were obtained in good to high yield (Table 4, entries 10–13). For carbamates 2h–2j (60°C; Table 4, entries 14–20) and carboxamides 2k–2l (90°C; Table 4, entries 21–22), a higher reaction temperature was required to promote hydroamination smoothly. On the other hand, vinyl arene 1c with an electron-donating group

required mild reaction conditions to avoid self-polymerization of 1c. The yield of 3cb was 20% at 20°C due to competitive undesired polymerization (Table 4, entries 23 and 24). Compound 3cb was obtained in 75% yield by performing the reaction of 1c at 8°C in dimethoxyethane (DME) (Table 4, entry 25).[13] The superiority of the hafnium catalyst over other catalysts was confirmed again in the reaction of 1c with 2b (Scheme 1). At 8°C, neither Bi(OTf)₃/4b[10] nor TfOH[7] gave the product 3cb; only Hf(OTf)₄/4b gave 3cb in good yield.[14,15]

We assume that the present hydroamination would proceed by a similar mechanism with either the bismuth or hafnium catalyst. On the basis of previous mechanistic studies of the hydroamination of 1,3-dienes with Bi(OTf)₃/ [Cu(CH₃CN)₄]PF₆,[10] a catalytic cycle for the present reaction is proposed in Scheme 2. A cationic bismuth and hafnium species, generated by anion exchange, is the active species (I). The amide coordinates to the cationic metal (II), and the catalyst activates vinyl arenes to generate a carbenium intermediate (III). Amide addition followed by protonolysis affords the product and regenerates the catalyst (I).
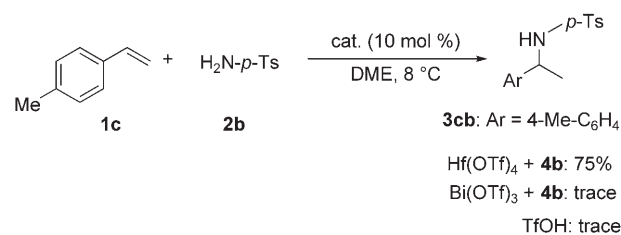
Scheme 1. Intermolecular hydroamination of electron-donating vinyl arene 1c with 2b using 10 mol% of Hf(OTf)₄, Bi(OTf)₃, or TfOH.
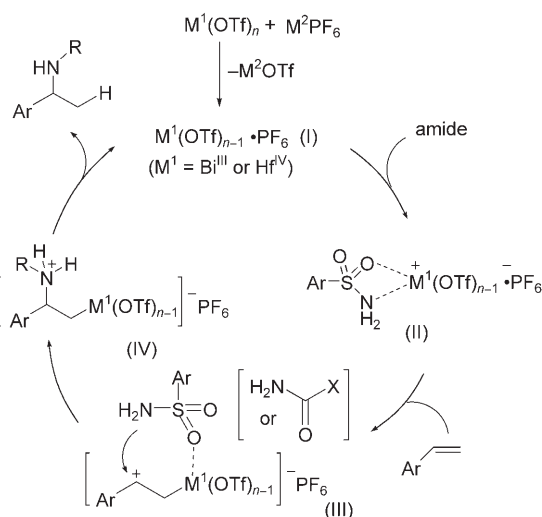
Scheme 2. Proposed catalytic cycle of hydroamination.

Conclusions

In summary, we have developed a bismuth- and hafnium-catalyzed intermolecular hydroamination of vinyl arenes with amides. The new $Hf(OTf)_4/[Cu(CH_3CN)_4]PF_6$ system has broader substrate generality than the previous bismuth catalyst, promoting the reaction of various vinyl arenes with sulfonamides, carbamates, and carboxamides at 8–90°C in 54–99% yield. Catalyst loading was successfully reduced to 0.3 mol% by using sulfonamide **2b** (TON up to 253). The present system is applicable to less-reactive vinyl arenes with electron-withdrawing groups. Further application of the hafnium catalyst is ongoing.

Experimental Section

General

Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer operating at 500 MHz for ^1H and 125.65 MHz for ^{13}C. Chemical shifts in $CDCl_3$ are reported downfield from TMS ($=0$) or relative to $CHCl_3$ (7.24 ppm) for ^1H NMR spectroscopy. For ^{13}C NMR spectroscopy, chemical shifts are reported relative to $CHCl_3$ (77.0 ppm) as an internal reference. ESI mass spectra were recorded on a Waters-ZQ4000 spectrometer. FAB and EI mass spectra were redorded on a JEOL JMS-700 or JMS-BU20 GCmate. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Reactions were carried out in dry solvents under an argon atmosphere unless otherwise stated. Compounds **3ae**, **3bh**, **3dh**, **3bi**, and **3di** are new compounds. All the other compounds synthesized herein are known compounds; see reference [5] and references therein.

Syntheses

Typical procedure (**3ab**): Anhydrous 1,4-dioxane (1.0 mL) was added to a mixture of $Hf(OTf)_4$ (23.4 mg, 0.03 mmol) and $[Cu(CH_3CN)_4]PF_6$ (11.2 mg, 0.03 mmol) in a test tube. After the mixture was stirred for 10 min at room temperature, **2b** (0.30 mmol) and then **1a** (0.60 mmol) were successively added. The reaction mixture was stirred at 25°C for 24 h. The mixture was diluted with diethyl ether (5 mL), and silica gel (≈ 3 g) was added to the mixture. After filtration and washing with dieth-

yl ether, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate $=8:1–6:1$) to give **3ab** (90%) as a colorless solid.

3ae: Colorless solid. IR (KBr): $\tilde{v}=623$, 701, 1062, 1163, 1318, 1403, 3261 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=1.67$ (d, $J=6.9$ Hz, 3H), 4.59 (dq, $J=6.9$, 6.9 Hz, 1H), 5.02 (br s, 1H), 7.01–7.03 (m, 2H), 7.12–7.16 (m, 3H), 7.56 (br d, $J=8.6$ Hz, 2H), 7.74 ppm (br d, $J=8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=23.6$, 54.1, 123.2 (q, $J_{C,F}=270$ Hz), 125.8, 126.1, 127.5, 127.6, 128.5, 133.8 (q, $J_{C,F}=31.7$ Hz), 141.2, 144.2 ppm; LRMS (ESI, methanol): $m/z=352$ $[M+Na]^+$; HRMS (EI): m/z calcd for $C_{14}H_{11}F_3NO_2S$: 314.0457 $[M-CH_3]^+$; found: 314.0448.

3bh: Colorless solid. IR (KBr): $\tilde{v}=763$, 835, 1012, 1039, 1253, 1417, 1493, 1746 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=1.56$ (d, $J=7.0$ Hz, 3H), 3.12–3.19 (m, 1H), 3.47–3.53 (m, 1H), 4.24 (ddd, 6.7, 8.5, 9.2 Hz, 1H), 4.28–4.35 (m, 1H), 5.19 (q, $J=7.0$ Hz, 1H), 7.26–7.30 (m, 2H), 7.32–7.36 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=16.3$, 39.9, 50.9, 61.9, 128.4, 128.8, 133.7, 138.1, 157.9 ppm; LRMS (ESI, methanol): $m/z=248$ $[M+Na]^+$; HRMS (FAB): m/z calcd for $C_{11}H_{13}ClNO_2$: 226.0629 $[M+H]^+$; found: 226.0631.

3dh: Colorless oil. IR (neat): $\tilde{v}=763$, 1006, 1252, 1417, 1488, 1746, 2922 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=1.56$ (d, $J=7.1$ Hz, 3H), 3.15 (ddd, 6.7, 8.5, 9.2 Hz, 1H), 3.49 (ddd, 6.7, 8.5, 9.2 Hz, 1H), 4.24 (ddd, 6.7, 8.5, 9.2 Hz, 1H), 4.31 (ddd, 6.7, 8.5, 9.2 Hz, 1H), 5.18 (q, $J=7.1$ Hz, 1H), 7.20–7.24 (m, 2H), 7.47–7.57 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=16.2$, 39.9, 50.9, 61.9, 121.8, 128.7, 131.7, 138.6, 157.8 ppm; LRMS (ESI, methanol): $m/z=292$ $[M+Na]^+$; HRMS (FAB): m/z calcd for $C_{11}H_{13}BrNO_2$: 270.0124 $[M+H]^+$; found: 270.0120.

3bi: Colorless solid. IR (KBr): $\tilde{v}=830$, 1012, 1069, 1261, 1550, 1694, 2984, 3313 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=1.45$ (d, $J=7.5$ Hz, 3H), 3.65 (s, 3H), 4.80 (br s, 1H), 4.90 (br s 1H), 7.24 (br d, $J=8.5$ Hz, 2H), 7.28–7.32 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=22.3$, 50.1, 52.1, 127.3, 128.7, 132.9, 142.2, 156.1 ppm; LRMS (ESI, methanol): $m/z=236$ $[M+Na]^+$; HRMS (FAB): m/z calcd for $C_{10}H_{13}ClNO_2$: 214.0629 $[M+H]^+$; found: 214.0632.

3di: Colorless solid. IR (KBr): $\tilde{v}=824$, 1009, 1070, 1261, 1541, 1694, 3316 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=1.45$ (d, $J=7.2$ Hz, 3H), 3.65 (s, 3H), 4.78 (br s, 1H), 4.91 (br s 1H), 7.18 (br d, $J=8.5$ Hz, 2H), 7.45 ppm (br d, $J=8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=22.3$, 50.1, 52.1, 121.0, 127.6, 131.7, 142.8, 156.1 ppm; LRMS (ESI, methanol): $m/z=280$ $[M+Na]^+$; HRMS (FAB): m/z calcd for $C_{10}H_{13}BrNO_2$: 258.0124 $[M+H]^+$; found: 258.0124.

Acknowledgements

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[15] The Hf(OTf)$_4$/[Cu(CH$_3$CN)$_4$]PF$_6$ system is not applicable to 4-methoxystyrene owing to competitive self-polymerization.