

Gold(I)-Catalyzed Intra- and Intermolecular Hydroamination of Unactivated Olefins

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Metal-catalyzed hydroamination of simple olefins is one of the important strategies to prepare nitrogen-containing molecules.^{1,2} Despite significant efforts that have been devoted into this idea,^{2–4} only a few examples of intermolecular hydroamination of unactivated olefins are known. On the basis of some recent studies,⁵ we envisioned that hydroamination of unactivated olefins might be catalyzed by gold complexes, as well. We report here the gold(I)-mediated hydroamination of inert olefins to afford acyclic or cyclic nitrogen-containing molecules. This discovery adds another new methodology into the growing list of reactions that can be catalyzed by gold ions.⁶

In preliminary experiments, we tested reactions between cyclohexene and various nitrogen nucleophiles. *p*-Toluenesulfonamide (TsNH₂) stands out as an excellent candidate for this reaction. *N*-cyclohexyl-*p*-toluenesulfonamide could be prepared in 90% isolated yield by reacting TsNH₂ with 4 equiv of cyclohexene in toluene with a catalytic amount (5 mol %) of Ph₃PAuOTf (generated

Table 1. Intermolecular Hydroamination of Olefins^a

Entry	Olefin	Nucleophile	Time(h)	Product	Yield(%) ^b
1	(1a)	TsNH ₂ (1b)	15		90(91) ^c
2 ^d	(1a)	TsNHCH ₃ (2b)	44		56
3 ^e	(1a)	RSO ₂ NH ₂ (3b)	15		89
4	(3a)	1b	20		83
5	(4a)	1b	14		51
6	(5a)	1b	16		56
7	(6a)	1b	14		95(93) ^c
8	(6a)	2b	48		55
9	(8a)	1b	14		85 ^f
10	(9a)	1b	38		51
11 ^g	(10a)	1b	15		89
12 ^g	(10a)	3b	15		80
13	(11a)	1b	48		44

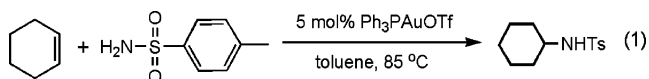
^a Reactions were conducted with 1 mmol of nucleophiles, 4 mmol of olefins (2.0–2.8 mmol could be recovered after the reaction in most cases), and 5 mol % of Ph₃PAuCl/AgOTf in 2 mL of toluene at 85 °C. ^b Isolated yield. ^c The yield in parentheses refers to a reaction performed without solvent. ^d At 95 °C. ^e R = MeOC₆H₄. ^f 9c:9c' = 2:1. ^g A 1:1 ratio of TsNH₂ and norbornene was used.

Table 2. Gold(I)-Catalyzed Intramolecular Hydroamination of Tosylated Amino Olefins^a

Entry	Substrate	Time(h)	Product	Yield(%) ^b
1		17		96
2 ^c		48		99
3		48		0
4		15		91
5		15		95
6		15		99
7		10		97

^a Reactions were conducted with 0.5 mmol of substrate and 5 mol % of Ph₃PAuCl/AgOTf in 2 mL of toluene at 85 °C. ^b Isolated yield. ^c Ns = 2-nitrobenzenesulfonate.

by mixing equal equivalents of Ph₃PAuCl and AgOTf) at 85 °C for 15 h (eq 1). With the use of other nitrogen-based molecules, such as amines, anilines, carboxyamides, carbamates, alkylsulfonamides, or sulfamates, the reactions gave none or very low yields of the desired products. Other Lewis acids, such as Zn(OTf)₂ and Cu(OTf)₂, could not catalyze the same reaction, and Sc(OTf)₃ gave less than 20% of the addition product under the same conditions.



This reaction works for a range of different olefins, as shown in Table 1. Terminal olefins can serve as good substrates to afford the Markovnikov addition products (Table 1, entries 6–9). *N*-methyl-*p*-toluenesulfonamide (2b) as well as *p*-methoxyphenylsulfonamide could be used as the nucleophiles (Table 1, entries 2, 3, 8, and 12). The β-hydride elimination step that typically leads to the unsaturated addition products with palladium-mediated reactions^{3,7} does not occur with the use of gold(I) catalyst. Intramolecular alkene hydroamination was also examined, and several *N*-tosylated γ-amino olefins were efficiently cyclized to afford pyrrolidines with gold(I) (Table 2). 2-Nitrobenzenesulfonamide could also be employed as an efficient nucleophile (Table 2, entry 2). Amides did not work as nucleophiles for this reaction (one example is shown in Table 2, entry 3). Preliminary studies indicate that carbamates also work as nucleophiles in intramolecular additions.

