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Hydrohydrazination of Arylalkynes Catalyzed by an Expanded Ring N-Heterocyclic Carbene (er-NHC) Gold Complex Under Solvent-Free Conditions

Oleg S. Morozov,[a] Pavel S. Gribanov,[a] Andrey F. Asachenko,[a,b] Pavel V. Dorovatovskii,[c] Victor N. Khrustalev,[d,e] Viktor B. Rybakov,[f] and Mikhail S. Nechaev[a,b,f,*]

[a] A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospect 29, Moscow, 119991, Russia
E-mail: m.nechaev@ips.ac.ru or m.s.nechaev@org.chem.msu.ru
[b] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 119991, Russia
[c] NRC Kurchatov Institute, Acad. Kurchatov Square 1, Moscow, 123182, Russia
[d] Department of Inorganic Chemistry, Peoples' Friendship University of Russia, Miklukho–Maklay Street 6, Moscow, 117198, Russia
[e] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, Moscow 119991, Russia
[f] M. V. Lomonosov Moscow State University, Leninskie Gory 1 (3), Moscow, 119991, Russia

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Abstract: [(THD-Dipp)AuOTf], supported by the strongly electron donating, sterically bulky THD-Dipp (1,3-bis(2,6-diisopropylphenyl)hexahydro-2*H*-1,3-diazepine-2-ylidene) seven-membered N-heterocyclic carbene ligand, efficiently promotes intermolecular addition of Ts- and Boc-hydrazine to arylalkynes under solvent-free conditions.

Keywords: alkynes; gold; hydrazine; hydroamination; N-heterocyclic carbenes

Introduction

Hydrazone derivatives are of great interest for synthetic organic chemistry as important building blocks.[1] Hydrazone moieties can be found in many compounds of biological interest.[2]

Aryl-, *N*-tosyl-, and *N*-Boc-hydrazones have found numerous applications in various organic transformations. Thus, aryl hydrazones are precursors for indoles obtained via hydrazone rearrangement in Fischer indole synthesis.[3] *N*-Tosylhydrazones are useful precursors for synthesis of alkenes via base-induced Bamford-Stevens[4] and Shapiro[5] reactions. Recent reports are devoted to the use of *N*-tosylhydrazones as safe precursors for diazo compounds in transition-metal-catalyzed cross-coupling reactions.[6] A metal-free C–C bond-forming reaction between tosylhydrazones and boronic acids was recently reported.[7] *N*-Boc-hydrazones have found applications as building blocks in heterocyclic synthesis[8] and as a directing groups in transition-metal-catalyzed dehydrogenative cross-coupling reactions via selective C–H bond activation.[9]

The most general method for the synthesis of hydrazones is the reaction of hydrazines with carbonyl compounds.[10] This method is inapplicable for synthesis of hydrazines bearing carbonyl or other electrophilic groups due to high nucleophilicity of both nitrogen atoms in hydrazine. Therefore, it is highly desirable to develop other atom-economical protocols that involves fewer synthetic steps and readily available starting materials for the preparation of hydrazones.

The alternative route for the synthesis of hydrazones is catalytic hydroamination of alkynes by hydrazine derivatives.[11] Gold(I) species are known to be efficient catalysts of inter- and intramolecular hydroamination of alkynes.[12] Bertrand et al.[13] have shown that gold(I) complexes featuring bulky cyclic (alkyl)-(amino)carbene (CAAC)[14] readily catalyze the addition of H_2NNH_2 to a variety of non-activated alkynes and allenes to afford a diverse array of acyclic and cyclic nitrogen-containing compounds. Recently, Ber-

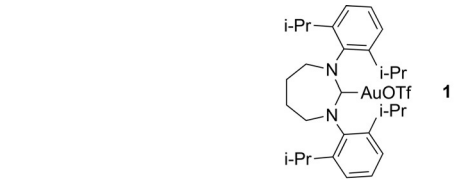
trand's[15] and Hashmi's[16] groups have shown that anti-Bredt NHC and saturated abnormal N-heterocyclic carbene (saNHC) gold(I) complexes promote the addition of hydrazine to terminal alkynes under mild conditions. Mechanisms of catalytic reactions were rationalized using DFT calculations.[17]

To date only a few examples of gold catalyzed hydrohydrazination of non-activated alkynes by phenylhydrazine (two examples),[18] and tosylhydrazide[19] have been reported. No examples of hydrohydrazination with *tert*-butyl carbazate (Boc-hydrazide) have been reported. Herein, we present a simple and versatile method for highly selective addition of nucleophilically deactivated hydrazine derivatives to non-activated arylalkynes. The catalytic reaction is mediated by a NHC supported gold complex under solvent-free conditions.

Results and Discussion

Er-NHCs surpass five-membered ring counterparts in donor properties and steric stabilization of metal complexes.[20] We have previously shown[21] that utilization of the seven-membered-ring carbene bearing bulky Dipp groups in combination with weakly coordinating anions such as $X^- = OTf^-$ or BF_4^- in [(THD-Dipp)AuX] (THD-Dipp = 1,3-bis(2,6-diisopropylphenyl)hexahydro-2*H*-1,3-diazepine-2-ylidene) results in extremely active catalytic systems for intramolecular hydroamination of 2-ethynylanilines leading to indoles under unprecedentedly mild conditions. This finding prompted us to investigate catalytic activity of such complexes in intermolecular hydrohydrazination of alkynes.

We were able to obtain X-ray quality single crystals of [(THD-Dipp)Au(OTf)] (**1**) (Figure 1).[22] Two experiments were made using a synchrotron and a more conventional single crystal diffractometer (for details see SI). Interestingly, the experiment using a diffractometer gave a more ordered structure ($R_1 = 0.0639$ *vs* 0.0755) than the synchrotron experiment. We suppose that it was due to different quality of crystals obtained under different conditions. Further, we will discuss the structure with a better R-factor. As expected, **1** adopts a linear geometry with an O1-Au1-C1 bond angle of 176.2(3)°. The Au1-O1 bond length of 2.112(9) Å shows a covalent bonding character between the gold and oxygen atoms. The Au1-C1 bond length is 1.936(8) Å. Au1-O1 and Au1-C2 distances lie in a range determined for related NHC gold complexes containing oxygen-coordinated ligands (the ranges of 2.019(7)–2.078(6) and 1.935(6)–2.006(17) Å, respectively).[23] The angle about the oxygen O1 atom (131.7(4)°) is significantly distorted from the idealized value of 109.5°, likely due to the combined steric reasons of the NHC and triflate ligands.



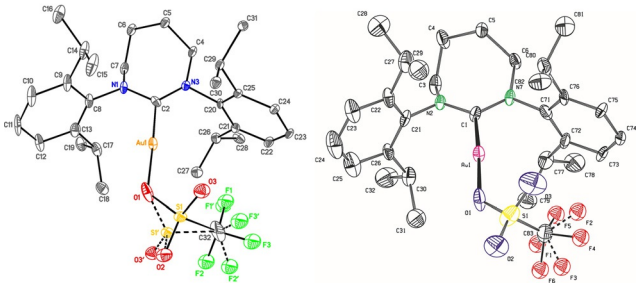
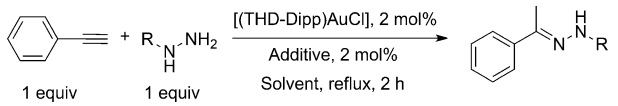


Figure 1. Molecular structure of (7-Dipp)Au(OTf) (**1**) obtained using a synchrotron (left) and a diffractometer (right) experiments. Anisotropic displacement ellipsoids are drawn at the 30% and 20%, respectively, for the structures left and right. An alternative position of the disordered triflate group with the lesser occupancy is depicted by dashed lines. Hydrogen atoms are omitted for clarity.

In the preliminary set of experiments we have found that [(THD-Dipp)AuCl] activated by AgOTf efficiently promotes addition of various hydrazines to phenylacetylene (Table 1, entries 1–5). It is worth noting that in the case of hydrazine hydrate only azine was formed, no hydrazone formation was observed. In all remaining cases, (*E*)-*N*-substituted hydrazones were the major products. The reaction proved to be highly sensitive to the choice of a solvent (entries 5–11) and the nature of weakly coordinating anion (entries 11–14). Non-activated complex exhibit virtually no activity (entry 15). The highest yield in the reaction of *p*-toluenesulfonylhydrazide with phenylacetylene was obtained when preformed complex [(THD-Dipp)AuOTf] was used as a catalyst (entry 16).

To determine the scope of the developed catalytic protocol we studied the addition of challenging substrates such as *p*-toluenesulfonyl hydrazide and *tert*-butyl carbazate to various aryl acetylenes (Table 2). Alkynes bearing electron-donating groups on benzene ring show moderately high activity with both hydrazine derivatives (entries 1, 2, 3, 5, 7). In sharp contrast, alkynes bearing electron-withdrawing groups, even as weak as Cl, give products in moderate yields (entries 6, 9). Sterically hindered alkynes give products in low yields (entries 4, 8). In the case of 2-ethynyl-1,3,5-trimethylbenzene **2j**, no formation of the products was observed (entry 10). It should be noted that in all cases hydrazones were obtained as (*E*)-isomers, and no formation of anti-Markovnikov addition products was observed.

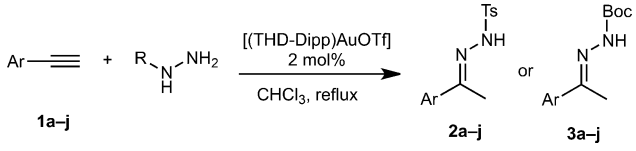
Table 1. Hydroamination of phenylacetylene.



Entry	$RNHNH_2$	Solvent	Additive	Yield[a]
1	N_2H_4*H_2O	EtOH	AgOTf	97 %[b]
2	$PhNHNH_2$	EtOH	AgOTf	98 %
3	2,4-di-NO_2-$PhNHNH_2$	EtOH	AgOTf	90 %
4	$BocNHNH_2$	EtOH	AgOTf	79 %
5	$TsNHNH_2$	EtOH	AgOTf	83 %
6	$TsNHNH_2$	Toluene	AgOTf	67 %
7	$TsNHNH_2$	MeOH	AgOTf	70 %
8	$TsNHNH_2$	THF	AgOTf	18 %
9	$TsNHNH_2$	1,4-dioxane	AgOTf	12 %
10	$TsNHNH_2$	MeCN	AgOTf	57 %
11	$TsNHNH_2$	$CHCl_3$	AgOTf	85 %
12	$TsNHNH_2$	$CHCl_3$	$AgBF_4$	80 %
13	$TsNHNH_2$	$CHCl_3$	$AgNTf_2$	35 %
14	$TsNHNH_2$	$CHCl_3$	$NaBAr^F_4$	60 %
15	$TsNHNH_2$	$CHCl_3$	–	<2 %
16	$TsNHNH_2$	$CHCl_3$	–	87 %[c]

[a] Isolated yield.
[b] Formation of (1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine was observed.
[c] [(THD–Dipp)AuOTf] used as a catalyst.

Table 2. Catalytic hydrohydrazination of terminal alkynes.[a]



Entry	Aryl	Isolated yield [%] $TsNHNH_2$	Isolated yield [%] $BocNHNH_2$
1	C_6H_5	87 (**2a**)	91 (**3a**)
2	4-Me-C_6H_4	76 (**2b**)	90 (**3b**)
3	4-MeO-C_6H_4	80 (**2c**)	80 (**3c**)
4	2-MeO-C_6H_4	46 (**2d**)	23 (**3d**)
5	4-PhO-C_6H_4	62 (**2e**)	76 (**3e**)
6	4-Cl-C_6H_4	52 (**2f**)	55 (**3f**)
7	4-Me_2N-C_6H_4	70 (**2g**)	68 (**3g**)
8	naphthyl	47 (**2h**)	27 (**3h**)
9	4-MeOOC-C_6H_4	41 (**2i**)	58 (**3i**)
10	2,4,6-triMe-C_6H_2	0 (**2j**)	0 (**3j**)

[a] Reaction conditions: 3 mmol of alkyne, 3 mmol of hydrazine derivative in 5 mL of $CHCl_3$, 2 mol % [(THD-Dipp)AuOTf], 1–6 h.

Development of solvent-free synthetic protocols is of great interest. Utilization of solvent-free technologies lead to more simple, productive, energy- and cost-effective, clean and safe chemical processes.[24] Optimization of solvent-free reaction conditions have been performed for hydrohydrazination of phenylacetylene with *p*-toluenesulfonyl hydrazide as a model system (for details see SI). Optimized conditions are the following: melting together the equimolar amount of an alkyne and a hydrazine derivative in presence of 0.25 mol % of [(THD-Dipp)AuOTf] at 100 °C under stirring. The reaction mixture appeared as a clear melt that slowly solidified. Solidification indicates the formation of the desired hydrazone.

Addition of *p*-toluenesulfonylhydrazide and *tert*-butyl carbazate to various alkynes **1a–n** was studied (Table 3). In all cases, high or near quantitative yields were obtained. Both $TsNHNH_2$ and $BocNHNH_2$ readily undergo addition to arylalkynes bearing donor, acceptor, as well as sterically bulky substituents. Products of addition of hydrazines to diphenylacetylene (**2m**, **3m**) and octyne-1 (**2n**, **3n**) were obtained in high yields as well. Thus, the solvent-free protocol is far more efficient than the solvent-mediated reaction. The advantages are: i. lower catalyst loading (0.25 mol % vs 2.0 mol %), ii. higher yields, iii. shorter reaction time, and iv. wider scope of arylalkyne substrates.

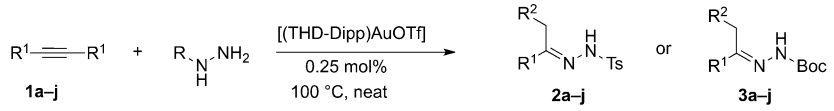
We studied the influence of catalyst loading on the yield of the reaction of 4-MeO-C_6H_4-C≡CH with R-$NH-NH_2$ (R = Ph, Ts, Boc; for details see SI). Experiments were set at catalyst concentrations 0.25, 0.1, and 0.01 mol %. At 0.01 mol % catalyst loading the obtained yields were very low. Although values of TONs are high (>1000), these numbers are meaningless since the reactions were far from completion. At 0.1 mol % catalyst loading the obtained yields were high: 98 %, 88 %, and 93 %, for R = Ph, Ts, and Boc, respectively. The respective calculated TONs were 980, 880, and 930. Such high values far exceed TONs reported previously for hydrohydrazination of aryl acetylenes.[18a,19]

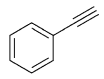
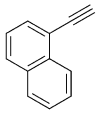
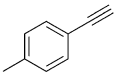
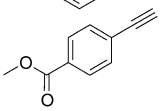
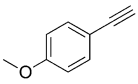
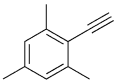
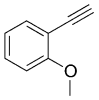
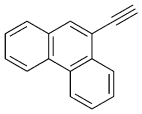
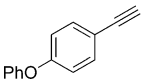
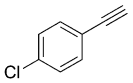
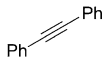
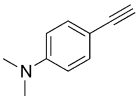
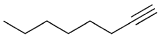
We have also found that for some substrates, reactions catalyzed by [(THD-Dipp)AuOTf] under solvent-free conditions do not stop at the formation of hydrazones. Thus, interaction of phenylacetylene with ethyl hydrazinecarboxylate leads to the formation of (*E*,*E*)-bis-(1-phenylethylidene)-hydrazine in 90 % yield (Scheme 1a). In the case where a carboethoxy moiety is attached to an alkyne, 3*H*-pyrazol-3-ones are formed in high yields (Scheme 1b).

Conclusions

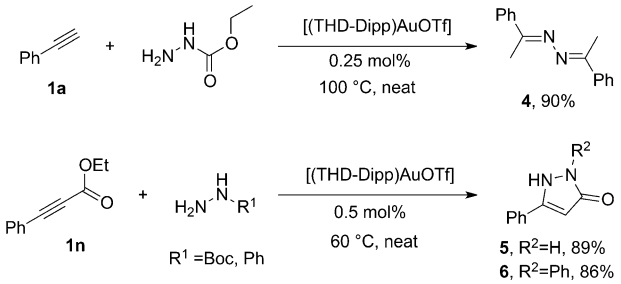
In conclusion, [(THD-Dipp)AuOTf] promotes the addition of hydrazines to non-activated alkynes leading to the formation of hydrazones with perfect Markovnikov regioselectivity in high yields. We have developed a simple and practical protocol for the preparation of tosyl- and Boc-protected hydrazones under

Table 3. Catalytic hydrohydrazination of alkynes under solvent-free conditions.[a]



Alkyne	$TsNHNH_2$	$BocNHNH_2$	Alkyne	$TsNHNH_2$	$BocNHNH_2$
	**2a**, 97%	**3a**, 95%		**2h**, 85%	**3h**, 86%
	**2b**, 98%	**3b**, 96%		**2i**, 88%	**3i**, 99%
	**2c**, 90%	**3c**, 89%		**2j**, 78%	**3j**, 87%[b]
	**2d**, 89%	**3d**, 81%[b]		**2k**, 89%	**3k**, 97%[b]
	**2e**, 82%	**3e**, 86%		**2l**, 92%	**3l**, 86%
	**2f**, 91%	**3f**, 97%		**2m**, 92%	**3m**, 96%
	**2g**, 77%	**3g**, 85%		**2n**, 75%[b]	**3n**, 76%[b]

[a] Isolated yields
[b] Mixture of (*E*)- and (*Z*)-isomers formed



Scheme 1. Reactions promoted by [(THD-Dipp)AuOTf].

solvent-free conditions without the need for an inert atmosphere. In addition, our method is in close agreement with the concept of "green" chemistry: (i) reaction proceeds with high atom economy (E factor = 0.02-0.27),[24] (ii) non-toxic derivatives of hydrazine are used, (iii) no solvent is used. We believe that our findings might lead to broader use of gold-mediated reactions in laboratory practice and in the development of "green" industrial technologies.

Experimental Section

General procedure for Table 1

Under aerobic condition 26.0 mg (0.04 mmol) of [(THD-Dipp)AuCl] was dissolved in 5 mL of appropriate solvent (see Table 1). Then 0.04 mmol of additive was added and the mixture was stirred for 5 min. To this solution phenylacetylene (204 mg, 2 mmol) and the hydrazine derivative (2 mmol) were added and the mixture was refluxed for 2 h. After cooling to room temperature, the solution was passed though thin pad of Silica gel to remove gold species, eluted with dichloromethane and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent EtOAc/hexane = 10:1, Silica gel 43–60 μm).

General procedure for hydroamination of alkynes in chloroform (Method A)

Under aerobic conditions to a solution of 3 mmol of alkyne, 3 mmol of hydrazine derivative in 5 mL of $CHCl_3$ 45.9 mg (2 mol%) of [(THD-Dipp)AuOTf] was added. The solution was then heated to reflux and stirred until reaction was complete by TLC (eluent EtOAc/hexane = 7:3, 1–6 h). After cooling to room temperature, the solution was passed though thin pad of Silica gel to remove gold species, eluted

with dichloromethane (10 mL) and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent EtOAc/hexane = 10:1, Silica gel 43–60 μm).

General procedure for hydroamination of alkynes under solvent free condition (Method B)

A 10 mL vial was charged with a magnetic stirring bar, 2 mmol of alkyne, 2 mmol of hydrazine derivative and 3.8 mg (0.25 mol%) of [(THD-Dipp)AuOTf] and put into pre-heated (100 °C) oil bath. Then the vial was sealed and the mixture was stirred until the reacion was complete (full solidification or TLC control). The crude product was purified by column chromatography (eluent EtOAc/hexane = 10:1, Silica gel 43–60 μm).

Acknowledgements

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